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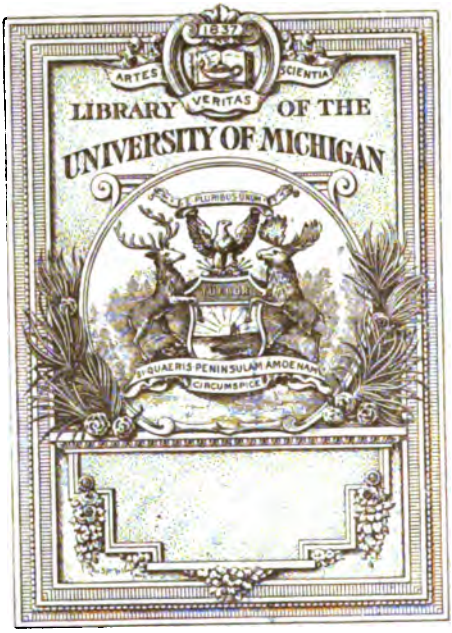

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A
TEXT-BOOK OF CHEMISTRY.

INTENDED FOR THE USE OF PHARMACEUTICAL
AND MEDICAL STUDENTS.

BY

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"THE NEWER REMEDIES."

BEING THE SECOND REVISED
AND ENLARGED EDITION OF

SADTLER AND TRIMBLE'S CHEMISTRY.

IN TWO VOLUMES.

VOL. II.—ANALYTICAL CHEMISTRY AND PHARMACEUTICAL ASSAYING.

PHILADELPHIA:
J. B. LIPPINCOTT COMPANY.
LONDON: 36 SOUTHAMPTON STREET, COVENT GARDEN.

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PREFACE TO THE SECOND EDITION.

In answering the demand for a new edition of this work, the authors desire to express their appreciation of the kind reception which was awarded to the book on its first issue and the continued favor which it has met.

They believed that a scientifically accurate and fairly complete work on chemistry, written from the stand-point of the pharmacist and giving especial attention to all compounds mentioned in the United States Pharmacopœia, would be of value not only to the student but to the practising pharmacist and physician, and are glad to know that this belief was justified.

The work, however, grew on their hands, and in consequence the first edition formed a large octavo of some 950 pages, the shape and bulk of the book making it inconvenient for many purposes.

To obviate this difficulty without sacrificing any of the features of the work that have proved valuable, the authors have now determined to issue the new edition in two volumes, one containing the Elementary Physics, Inorganic and Organic Chemistry, which together form the basis of the regular course of chemical instruction in our pharmaceutical and medical schools, and the other containing the Qualitative and Quantitative Analyses and Pharmaceutical Assaying found in the previous edition, together with a new section on Urinary Analysis and a few selected topics of importance to the practising pharmacist or physician, such as Water and Milk Analyses. They believe that in this way they will not only make the book more convenient to handle, but will give it a wider field of usefulness and greater value to students and practitioners alike.

Volume I. has been carefully revised and much new matter incorporated, especially in Part IV. under Organic Chemistry.

Several additional illustrations have been inserted, such as those in illustration of the views now held on stereo-chemistry and the new methods for the determination of molecular weights of organic compounds.

Some few sections on the technical applications of organic chemistry which were found in the first edition have been omitted, as it was thought that they might be spared from a book intended to bear specially upon pharmaceutical chemistry.

Volume II. has been almost entirely rewritten and much enlarged from what constituted Part V. of the original book. The part on Quantitative Analysis has been expanded and made serviceable as the basis of a fuller laboratory course on this subject; Pharmaceutical Assaying has been made to cover all the valuable assays of the United States Pharmacopœia; and, as already stated, the sections on Urinary Analysis and Milk and Water Analyses have been added.

The authors wish to express their especial indebtedness to Mr. Josiah C. Peacock for much valuable assistance in the preparation of Volume II., as, owing to the protracted illness of one of us, this part of the work was finished by him.

They desire also to acknowledge the assistance of Miss Florence Yaple, who undertook the compilation of the index for the book.

SAMUEL P. SADTLER,
HENRY TRIMBLE.

POSTSCRIPT.—The death of Professor Henry Trimble, which took place August 24, 1898, while Volume II. was passing through the press, made it desirable that some provision for the future work on this book should be made. The surviving author is glad to be able to state, therefore, that he has associated with himself Dr. Virgil Coblentz, Professor of Chemistry and Physics in the New York College of Pharmacy, who from this time on will share the editorship of the book with him. While no radical change in the plan of the work is contemplated, the authors purpose to keep it in all respects abreast of the latest developments of chemical science.

SAMUEL P. SADTLER.
VIRGIL COBLENTZ.

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ANALYTICAL CHEMISTRY AND PHARMACEUTICAL ASSAYING.

PART I.

QUALITATIVE ANALYSIS.

CHAPTER I.

PRELIMINARY CONSIDERATIONS.

QUALITATIVE analysis may be appropriately considered under two heads, (1) the behavior of known elements and compounds towards certain other known elements and compounds, termed reagents, and (2) the separation or detection of unknown elements and compounds by means of these reagents. The latter is frequently accomplished by converting the element sought into some well-known and characteristic compound.

A reagent, then, is a substance applied to another in order to separate it, or to produce with it some distinguishing result.

Reagents may be applied in two ways, wet and dry ; the former usually consists in adding a solution of the reagent to a solution of the substance under investigation. This method of employing reagents is almost exclusively used in pharmaceutical analysis.

The list of reagents and test-solutions given in the United States Pharmacopœia will be found to supply most of the needs for a study of qualitative analysis.

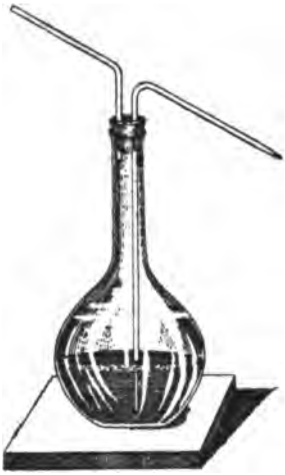
Precipitation is the process performed most frequently in chemical analysis. It consists in adding a reagent, drop by drop, to a solution of the substance under examination until, after agitating and sometimes warming, no further precipitate is produced.

Filtration is the natural sequence of precipitation, and is most readily accomplished by pouring the mixture on a plain filter,—

that is, one which has been folded twice and opened so as to form a cone; this cone should be placed in a funnel large enough to prevent the filter projecting above its edge.

The result of filtration is the separation of a mixture into a *precipitate* and a *filtrate*. Filtration should not be performed immediately after the reagent has been added, but a few minutes should be allowed to elapse for complete precipitation to take place, and the filtrate should always be tested with a little more of the reagent in order to determine if the precipitation has been complete.

FIG. 1.



Wash-bottle.

Precipitates, as a rule, should be well washed with distilled water; this is accomplished by the use of a wash-bottle, illustrated in Fig. 1. By blowing air into the shorter tube a jet of water is forced from the longer one, and this jet may be directed on any part of the precipitate. It sometimes prevents the washings from coming through cloudy to allow all of the liquid on the precipitate to drain through before adding more. In qualitative analysis it is not necessary to save all the washings.

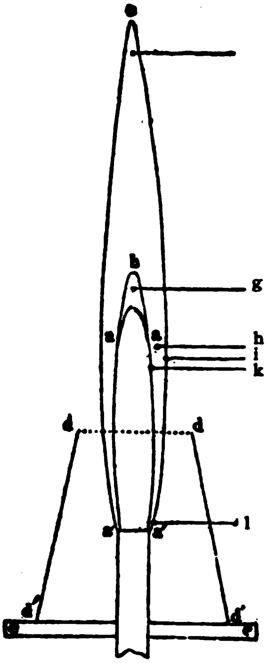
Reagents in the dry way are generally applied with the aid of heat. This is usually accomplished by heating the substance in a borax or microcosmic-salt bead or on charcoal.

The process by which a color is imparted to the non-luminous flame of a Bunsen burner, when a substance on platinum wire is held therein, may also be considered to belong to this method. For treatment on charcoal a blowpipe is necessary, but borax beads may be sufficiently heated in the Bunsen burner flame. To fully describe the structure of this flame, Fig. 2 is here given. The inner cone terminates at or near *a a*, the flame envelope extends from *a′ a′* to *c*; *f* is the upper oxidizing flame, *g* is the upper reducing flame, and is in the luminous part *a a b*, *b* is the point of highest temperature, *i* is the lower oxidizing flame, *k* is the lower reducing flame, and *l* is the base of the flame.

The blowpipe flame is best illustrated by Fig. 3, in which *a* is the reducing flame, and *b* the point of most energetic oxidation.

The flame colorations are best obtained by use of the platinum wire which is conveniently attached to a glass handle, as shown in Fig. 4. This wire, with some of the substance adhering to it, should be brought into the flame a little above the base, *l*, Fig. 2. That part of the wire nearest the glass handle should be introduced first, and the wire drawn through to the loop at the end. In this way the substance is volatilized and imparts color to the whole length of the flame from *l* to *c*. To clean the wire it should be alternately dipped in distilled water and drawn through the flame at *g*.

FIG. 2.



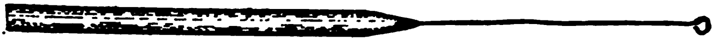
Gas flame.

FIG. 3.

Blowpipe flame.

Litmus paper is usually employed to ascertain if a liquid is acid, alkaline, or neutral. Acids turn the color of blue litmus paper red ; alkalies change the color of red litmus paper to blue ; neutral solutions do not affect either color.

FIG. 4.



Platinum wire.

When precipitates are to be fused with other substances, preparatory to further work upon them, the mixture should be placed upon a platinum foil whose edges have been bent upward, and this supported upon a triangle. Heat should then be cautiously applied, and gradually increased until uniform liquefaction has been produced. Decantation is the process of pouring off a clear supernatant liquid from a precipitate.

Analytical chemistry should be studied with the assistance of a competent instructor whenever that is possible. To those, however, who may be under the necessity of undertaking the study alone some simple directions may be useful.

In order to separate and detect the different elements, one should first make a practical study of them and their behavior towards reagents.

In commencing the analysis of the first group, therefore, the action of a few reagents should be tried on a salt of potassium preferably the chloride. In other words, the student should perform the reactions given under potassium, sodium, lithium, and ammonium, as described in the text. Having acquired a thorough knowledge of the behavior of the salts of these elements towards certain reagents, he is prepared to try the same reagents on unknown solutions containing salts of this group. He should have some one else to furnish him with these solutions, so that he may be literally working on unknown substances. When the material taken for analysis is in the form of a liquid, it is usually described as the *original solution.*

After a thorough knowledge of the first group has been acquired, which may usually be accomplished by the analysis of from three to five unknown solutions, the student is prepared to undertake the study of the second group. This is done, as with the first group, by performing the reactions with known solutions, and then detecting unknown bases. When the second group is completed, a number of solutions containing salts of both groups should be analyzed. In this way one group is added at a time until the seven groups of bases have been studied. The acids are then taken up in like manner, and, finally, unknown substances are examined for both bases and acids.

It is still more important that the student should be under the guidance of a competent instructor when he commences the study of quantitative analysis.

The most important rules to be observed in the practical study of chemistry are : to avoid all feverish hurry ; to add no reagent until time has been taken to understand the purpose for which it is added ; to remove from the table, as soon as any part of an operation is completed, the materials concerned in it ; to clean the vessels in which the substances were contained ; to observe the strictest care and neatness in all manipulations ; and, finally, to keep a complete record of all observations made and work performed.

CHAPTER II.

THE REACTIONS AND DETECTION OF BASES.

Group I. Potassium, Sodium, Lithium, Ammonium.

REACTIONS OF SOLUBLE SALTS OF POTASSIUM.

Use a 5-per-cent. solution of potassium chloride, KCl.

1. $PtCl_4$ added to some of the above solution of KCl causes a yellow, crystalline precipitate of **potassium platinic chloride,** K_2PtCl_6,* soluble in excess of water.

$$2KCl + PtCl_4 = K_2PtCl_6.$$

2. $Co_2(NO_2)_6 6NaNO_2$ produces in cold solutions a yellow, crystalline precipitate of **potassium cobaltic nitrite,** $K_6Co_2(NO_2)_{12}$, soluble in HCL, HNO_3, or H_2SO_4, but insoluble in $HC_2H_3O_2$.

$$6KCl + Co_2(NO_2)_6 6NaNO_2 = K_6Co_2(NO_2)_{12} + 6NaCl.$$

Alkaline solutions should be acidified with acetic acid previous to adding the reagent, and CO_2, if present, allowed to escape.

3. $H_2C_4H_4O_6$, in concentrated solution, added to a solution of a salt of potassium, produces a white, crystalline precipitate of **acid potassium tartrate,** $KHC_4H_4O_6$, soluble in excess of water, readily in hot water, acids, or potassium hydrate.

$$KCl + H_2C_4H_4O_6 = KHC_4H_4O_6 + HCl.$$

4. $C_6H_2(NO_2)_3OH$, in saturated solution, forms a yellow, crystalline precipitate of **potassium picrate,** $C_6H_2(NO_2)_3OK$

$$KCl + C_6H_2(NO_2)_3OH = C_6H_2(NO_2)_3OK + HCl.$$

5. A fragment of a potassium salt, on the loop of a platinum wire held in the non-luminous flame of a Bunsen gas-lamp, imparts a **violet** color. Organic matter also colors the flame violet; hence it should be removed by ignition before testing for potassium. This reaction is also interfered with by the presence of sodium salts, which color the flame yellow. The yellow rays

---

* Agitation by stirring with a glass rod facilitates the formation of this and the following precipitates of this element, while the addition of alcohol serves to render the precipitation more complete. The precipitates from the several reactions under potassium should be preserved to compare with those obtained from ammonium, that the great similarity may be noted.

of sodium may be excluded by viewing the flame through blue glass.

6. Potassium salts are not volatile at a low red heat, but are slowly volatilized at a white heat.

REACTIONS OF SOLUBLE SALTS OF SODIUM.

Use a 1-per-cent. solution of sodium chloride, $NaCl$.

1. Sodium salts color the non-luminous flame **yellow.**

So delicate is this reaction that the merest traces of the element are revealed by it, and even the presence of much larger quantities of potassium salts do not render it less effective.

It is particularly characteristic of these yellow rays that they do not pass through a blue medium; consequently, in the application of the flame test, the yellow color may be excluded by viewing the flame through a blue glass (tinted with cobalt oxide), which thus serves to render the violet color imparted by potassium salts still more distinct.

2. The salts of sodium are not volatile at a low red heat, but are slowly volatilized at a white heat.

REACTIONS OF SOLUBLE SALTS OF LITHIUM.

Use a 2-per-cent. solution of lithium chloride, $LiCl$.

1. Na_2HPO_4 produces, on boiling, a white precipitate of **lithium phosphate,** Li_3PO_4.

$$3LiCl + Na_2HPO_4 = Li_3PO_4 + 2NaCl + HCl.$$

This reaction takes place more readily when the solution is first made alkaline with $NaOH$ or NH_4OH.

2. Lithium salts impart an intense **crimson** color to the non-luminous flame. This is more or less interfered with by sodium salts, but the yellow color of sodium may be excluded by **ordinary** blue glass, which, if not too dark, will allow the crimson rays of lithium to pass through. These must not be confused with the violet potassium rays, which will pass through a **deep** blue glass.

3. Lithium salts are not volatile at a low red heat, but are slowly volatilized at a white heat.

REACTIONS OF SOLUBLE SALTS OF AMMONIUM.

Use a 5-per-cent. solution of ammonium chloride, NH_4Cl.

1. $PtCl_4$ produces a yellow, crystalline precipitate of **ammonium platinic chloride,** $(NH_4)_2PtCl_6$.

2. $Co_2(NO_2)_6 6NaNO_2$ causes in cold solutions a yellow, crystalline precipitate of **ammonium cobaltic nitrite,** $(NH_4)_6Co_2(NO_2)_{12}$, soluble in HCL, HNO_3, or H_2SO_4, but insoluble in $HC_2H_3O_2$.

3. $H_2C_4H_4O_6$ produces a white, crystalline precipitate of **acid ammonium tartrate,** $NH_4HC_4H_4O_6$, soluble in excess of water, readily in hot water, acids, or ammonium hydrate.

4. $C_6H_2(NO_2)_3OH$, in saturated solution, forms in solutions of salts of ammonium a yellow, crystalline precipitate of **ammonium picrate,** $C_6H_2(NO_2)_3O(NH_4)$.

5. NaOH, added to the ammonium chloride solution and the mixture heated, causes the evolution of **ammonia,** NH_3.

$$NH_4Cl + NaOH = NH_3 + NaCl + H_2O.$$

NH_3 is recognized by its odor, by holding near a glass rod moistened with HCl, which will produce dense white fumes of NH_4Cl, or by holding in the mouth of the tube a strip of moistened red litmus paper, which will be immediately turned blue by the alkaline vapor, in which form the NH_3 exists.

6. Ammonium salts are volatile at a low red heat. In this respect they are different from all the other members of this group.

DIRECTIONS FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP I.

To a small portion of the original solution add NaOH and heat. NH_3 will be given off if ammonium salts are present, and may be recognized by its odor or by its action on moistened red litmus paper, which is turned blue by it. Care must be taken, in this test, to prevent any of the alkaline liquid coming in contact with the paper through boiling or spurting, as it would likewise cause a blue color.

Dip a loop of platinum wire in the original solution and then bring it into the non-luminous flame, in order to obtain evidence of the presence or absence of Na and Li.

To test for potassium in the presence of ammonium salts, and for lithium in the presence of an excess of sodium salts, add to some of the original solution Na_2HPO_4 and NaOH, boil until the steam is free from alkaline reaction, and if necessary add more NaOH to keep the liquid in the dish alkaline, in order to completely expel the ammonia of ammonium salts, then filter.

Precipitate Li.	**Filtrate K.**
WHITE. **Wash with hot water containing NH_4OH until the washings show no more yellow flame from sodium salts, then dissolve the ppt. in HCl and apply flame test.** **Crimson color indicates Li.**	**Acidify with $HC_2H_3O_2$, allow to cool and cease effervescing, then add $Co_2(NO_2)_6.6NaNO_2$.** **Yellow ppt. indicates K.**

Group II. Barium, Strontium, Calcium, Magnesium.

REACTIONS OF SOLUBLE SALTS OF BARIUM.

Use a 5-per-cent. solution of barium chloride, $BaCl_2.2H_2O$.

1. H_2SO_4 produces an immediate precipitation of white **barium sulphate,** $BaSO_4$, insoluble in boiling HCl or HNO_3.

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

2. K_2CrO_4, even in dilute solutions, causes a yellow precipitate of **barium chromate,** $BaCrO_4$, soluble in HCl or HNO_3, but insoluble in $HC_2H_3O_2$.

$$BaCl_2 + K_2CrO_4 = BaCrO_4 + 2KCl.$$

3. $(NH_4)_2CO_3$ precipitates white **barium carbonate,** $BaCO_3$, soluble in $HC_2H_3O_2$.

$$BaCl_2 + (NH_4)_2CO_3 = BaCO_3 + 2NH_4Cl.$$

4. $(NH_4)_2HPO_4$ produces a white precipitate of **barium phosphate,** $BaHPO_4$, soluble in $HC_2H_3O_2$ or HCl.

$$BaCl_2 + (NH_4)_2HPO_4 = BaHPO_4 + 2NH_4Cl.$$

5. $(NH_4)_2C_2O_4$ causes a white precipitate of **barium oxalate,** BaC_2O_4, slightly soluble in $HC_2H_3O_2$. This precipitation will not take place in very dilute solutions.

$$BaCl_2 + (NH_4)_2C_2O_4 = BaC_2O_4 + 2NH_4Cl.$$

6. The salts of barium impart a **green** color to the non-luminous flame.

REACTIONS OF SOLUBLE SALTS OF STRONTIUM.

Use a 5-per-cent. solution of strontium nitrate, $Sr(NO_3)_2$.

1. H_2SO_4 forms a white precipitate of **strontium sulphate,** $SrSO_4$, immediately if the solution be strong, but not until after some time if it be very dilute.

2. K_2CrO_4 produces no precipitate in the presence of $HC_2H_3O_2$, but if the solution be made alkaline with KOH, a yellow precipitate of **strontium chromate,** $SrCrO_4$, falls.

3. $(NH_4)_2CO_3$ produces a white precipitate of **strontium carbonate**, $SrCO_3$, soluble in $HC_2H_3O_2$.

4. $(NH_4)_2HPO_4$ forms a white precipitate of **strontium phosphate**, $SrHPO_4$, soluble in $HC_2H_3O_2$ or HCl.

5. $(NH_4)_2C_2O_4$ causes the precipitation of white **strontium oxalate**, SrC_2O_4, sparingly soluble in $HC_2H_3O_2$, but readily soluble in HCl.

6. The salts of strontium impart an **intense red** color to the non-luminous flame.

Reactions of Soluble Salts of Calcium.

Use a 5-per-cent. solution of anhydrous calcium chloride, $CaCl_2$.

1. H_2SO_4, in moderately dilute solution, forms a white precipitate of **calcium sulphate**, $CaSO_4$, soluble in excess of water.

2. $(NH_4)_2CO_3$ produces a white precipitate of **calcium carbonate**, $CaCO_3$, soluble in $HC_2H_3O_2$. This precipitation is not complete unless the mixture is boiled.

3. $(NH_4)_2HPO_4$ causes the precipitation of white **calcium phosphate**, $CaHPO_4$, soluble in $HC_2H_3O_2$ or HCl.

4. $(NH_4)_2C_2O_4$ produces a white precipitate of **calcium oxalate**, CaC_2O_4, insoluble in $HC_2H_3O_2$, but soluble in HCl.

5. The salts of calcium impart a **yellowish-red** color to the non-luminous flame.

Reactions of Soluble Salts of Magnesium.

Use a 5-per-cent. solution of magnesium sulphate, $MgSO_4 \cdot 7H_2O$.

1. $(NH_4)_2CO_3$ causes a white precipitate of **magnesium ammonium carbonate**, $MgCO_3(NH_4)_2CO_3$.

$$MgSO_4 + 2(NH_4)_2CO_3 = MgCO_3(NH_4)_2CO_3 + (NH_4)_2SO_4.$$

Heat facilitates the precipitation. The compound is soluble in NH_4Cl, and by preceding the addition of the reagent by that of this substance a much smaller quantity will suffice to prevent the formation of the precipitate than will be required to dissolve it after once formed.

2. KOH, NaOH, or NH_4OH produces a white precipitate of **magnesium hydrate**, $Mg(OH)_2$, soluble in NH_4Cl.

$$MgSO_4 + 2KOH = Mg(OH)_2 + K_2SO_4.$$

3. $(NH_4)_2HPO_4$ with NH_4Cl and NH_4OH precipitates white, crystalline **magnesium ammonium phosphate**, $Mg(NH_4)\cdot$

PO_4, slightly soluble in water, but almost insoluble in water containing NH_4OH.

$$MgSO_4 + NH_4OH + (NH_4)_2HPO_4 = Mg(NH_4)PO_4 + (NH_4)_2SO_4 + H_2O.$$

Violent agitation or stirring assists in the formation of this precipitate.

$(NH_4)_2HAsO_4$, under similar circumstances, forms white, crystalline **magnesium ammonium arsenate**, $Mg(NH_4)AsO_4$.

NH_4Cl takes no part in the reaction, except to prevent the precipitation of $Mg(OH)_2$.

4. The salts of magnesium do not impart color to the flame.

CHART FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP II.

<table>
<tr><td colspan="4">Add to the original solution NH_4Cl, NH_4OH, and $(NH_4)_2CO_3$, boil and filter.</td></tr>
<tr><td colspan="3">Precipitate Ba, Sr, Ca.
Wash, dissolve in $HC_2H_3O_2$, dilute with H_2O, add K_2CrO_4, and filter.</td><td rowspan="3">Filtrate Mg.
Allow to cool, add $(NH_4)_2HPO_4$, and agitate. White, crystalline ppt. indicates Mg.</td></tr>
<tr><td rowspan="2">Ppt. Ba.
Yellow.</td><td colspan="2">Filtrate Sr, Ca.
Add very dilute H_2SO_4, allow to stand for 10 minutes, and filter.</td></tr>
<tr><td>Ppt. Sr.
White.
Wash, moisten with HCl, and confirm by flame test.</td><td>Filtrate Ca.
Add NH_4OH in excess and $(NH_4)_2C_2O_4$. White precipitate indicates Ca.</td></tr>
</table>

That the student may become acquainted with the method of analysis by this and subsequent charts the following explanation is given, in the belief that a thorough study of it will enable him to understand all the charts which follow, as they are simply enlargements of this scheme.

To a convenient quantity of the original solution in a test-tube add an equal volume of a 10-per-cent. solution of NH_4Cl, close and invert the tube so as to thoroughly mix the contents, add NH_4OH in excess (or until, after mixing, the solution smells distinctly of it), then add $(NH_4)_2CO_3$, and, if a precipitate is formed, boil, and continue the addition of this reagent until the precipitation is completed, then filter.

We suppose all four of the bases under consideration to be present in the solution until their absence is proven; so by the foregoing treatment we separate them into two forms,—an insoluble part, called a *precipitate*, and consisting of Ba, Sr, and Ca as carbonates, and a liquid portion, called a *filtrate*, and containing Mg as carbonate, to keep which from precipitating the NH_4Cl is added.

A few drops more of $(NH_4)_2CO_3$ should be added to the filtrate and the whole again boiled, to make sure that all the carbonates of Ba, Sr, and Ca have been precipitated. If this is found to be the case, $(NH_4)_2HPO_4$ is added to the cooled filtrate, when, if Mg be present, a white, crystalline precipitate of $Mg(NH_4)PO_4$ will form.

The precipitate of the carbonates of Ba, Sr, and Ca, after being washed by forcing a jet of water from the wash-bottle on it, is dissolved in $HC_2H_3O_2$, which is distributed in drops upon the filter. Effervescence arises from the action of the $HC_2H_3O_2$ in decomposing the carbonates to form soluble acetates of Ba, Sr, and Ca. The solution so obtained is allowed to pass through the filter, which to prevent loss of material is afterwards washed with water; the latter being collected with the $HC_2H_3O_2$ solution, serves the additional purpose of diluting it.

To this solution a few drops of K_2CrO_4 are added. If Ba is present a yellow precipitate is produced, in which case sufficient of the K_2CrO_4 should be added to impart its yellow color to the supernatant liquid, thus signifying the complete precipitation of the Ba as $BaCrO_4$. The mixture is then filtered; this again divides the material into a precipitate and a filtrate, the former indicating Ba, and the latter containing Sr and Ca. To this filtrate very dilute H_2SO_4 (made by adding a small quantity of H_2SO_4 to about 20 times its volume of water) is added, the mixture allowed to stand for 10 minutes for the $SrSO_4$ to form and subside, and then filtered, whereby another precipitate, consisting of Sr as $SrSO_4$, and a filtrate containing the Ca are obtained.

The precipitate is washed well with water, then moistened with a drop of HCl (which serves to render it somewhat more volatile), and confirmed by holding it upon a platinum wire in the non-luminous flame, which will be colored intense red if Sr be present. To the filtrate from the $SrSO_4$ precipitate add NH_4OH in excess, and then $(NH_4)_2C_2O_4$, when, if the solution contains Ca, a white precipitate of CaC_2O_4 will be produced.

CHART FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF ALL THE FOREGOING ELEMENTS.

<table>
<tr><td colspan="6">Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Add to the original solution NH_4Cl, NH_4OH, and $(NH_4)_2CO_3$, boil and filter.</td></tr>
<tr><td colspan="3">Precipitate Ba, Sr, Ca.
Wash, dissolve in $HC_2H_3O_2$, dilute with H_2O, add K_2CrO_4, and filter.</td><td colspan="3">Filtrate Mg, K, Na, Li, NH_4.
Allow to cool, add $(NH_4)_2HPO_4$, agitate, and filter.</td></tr>
<tr><td rowspan="3">Ppt. Ba.
Yellow.</td><td colspan="2">Filtrate Sr, Ca.
Add very dilute H_2SO_4, allow to stand, and filter.</td><td rowspan="3">Ppt. Mg.
White, crystalline.</td><td colspan="2">Filtrate K, Na, Li, NH_4.
Add Na_2HPO_4 and NaOH, boil to a small bulk and until all NH_3 has been expelled, filter.</td></tr>
<tr><td rowspan="2">Ppt. Sr.
White. Confirm by flame test.</td><td rowspan="2">Filtrate Ca.
Add NH_4OH until alkaline, and then $(NH_4)_2C_2O_4$. White ppt.</td><td rowspan="2">Ppt. Li.
White. Confirm by flame test.</td><td>Filtrate K, Na.
Acidify with $HC_2H_3O_2$ and add $Co_2(NO_2)_6 \cdot 6NaNO_2$. Yellow ppt. indicates K.</td></tr>
<tr><td>Test for Na and NH_4 in the original solution.</td></tr>
</table>

Group III. Manganese, Zinc, Cobalt, Nickel.

REACTIONS OF SOLUBLE SALTS OF MANGANESE.

Use a 2-per-cent. solution of manganous sulphate, $MnSO_4 \cdot 4H_2O$.

1. NH_4HS, in neutral or alkaline solution, precipitates flesh-colored **manganous sulphide**, MnS, which on exposure to air becomes brown. MnS is soluble in HCl, HNO_3, or H_2SO_4.

$$MnSO_4 + 2NH_4HS = MnS + (NH_4)_2SO_4 + H_2S.$$

2. When $NH_4C_2H_3O_2$ is present and H_2S is added, MnS is formed, but is held in solution by the $HC_2H_3O_2$ set free in the reaction.

$$MnSO_4 + 2NH_4C_2H_3O_2 + H_2S = MnS + (NH_4)_2SO_4 + 2HC_2H_3O_2.$$

If this solution is made alkaline with NH_4OH, MnS falls.

NH_4Cl facilitates the separation of MnS, while the salts of the organic acids and excess of NH_4OH retard it.

3. KOH or NaOH produces a whitish precipitate of **manganous hydrate,** $Mn(OH)_2$, insoluble in excess of the reagent.

$Mn(OH)_2$ rapidly becomes brown, owing to its conversion into **manganic hydrate,** $Mn_2(OH)_6$, by absorption of oxygen from the air.

4. NH_4OH likewise precipitates $Mn(OH)_2$, and in excess redissolves it, but not $Mn_2(OH)_6$. As with $Mg(OH)_2$, this precipitation is prevented by the previous addition of NH_4Cl.

5. $(NH_4)_2CO_3$ produces a white precipitate of **manganous carbonate,** $MnCO_3$, soluble in excess in the cold, but reprecipitated on warming.

6. HNO_3 and Pb_3O_4 will, on heating and allowing the precipitate to subside, impart to the supernatant liquid a red color, due to **permanganic acid,** $H_2Mn_2O_8$.

$$2MnSO_4 + 5Pb_3O_4 + 26HNO_3 = H_2Mn_2O_8 + 13Pb(NO_3)_2 + 2PbSO_4 + 12H_2O.$$

Hydrochloric acid and chlorides interfere with this reaction, and must be expelled by evaporating twice to dryness with HNO_3. This is known as Crum's process for detecting manganese. The PbO_2 is the active part of Pb_3O_4.

7. A fragment of a manganese salt fused on platinum foil with 1 part KNO_3, and 2 parts K_2CO_3 will form a green mass containing **potassium manganate,** K_2MnO_4.

$$3MnSO_4 + 4KNO_3 + 4K_2CO_3 = 3K_2MnO_4 + 3K_2SO_4 + 2N_2O_3 + 4CO_2.$$

8. A borax bead (formed by fusing on the loop of a platinum wire some calcined borax until it becomes a clear glass), with a manganese compound, in the oxidizing blowpipe flame, becomes **violet** while hot and a fine **amethyst** color on cooling.

REACTIONS OF SOLUBLE SALTS OF ZINC.

Use a 2-per-cent. solution of zinc sulphate, $ZnSO_4.7H_2O$.

1. H_2S, in the presence of $NH_4C_2H_3O_2$, causes a white precipitate of **zinc sulphide,** ZnS, insoluble in $HC_2H_3O_2$ or KOH, but readily soluble in HCl or HNO_3.

2. NH_4HS produces the same precipitate of ZnS.

3. KOH, NaOH, or NH_4OH gives a white precipitate of **zinc**

hydrate, $Zn(OH)_2$, readily soluble in excess of the reagent, forming **zincates,** as, for instance, $Zn(OK)_2$.

$$Zn(OH)_2 + 2KOH = Zn(OK)_2 + 2H_2O.$$

These compounds are decomposed on boiling, $Zn(OH)_2$ being again precipitated, or by NH_4HS, ZnS resulting.

4. $(NH_4)_2CO_3$ forms a white precipitate of **basic zinc carbonate,** $(ZnCO_3)_2(Zn(OH)_2)_3$, readily soluble in excess.

$$5ZnSO_4 + 5(NH_4)_2CO_3 + 3H_2O = (ZnCO_3)_2(Zn(OH)_2)_3 + 5(NH_4)_2SO_4 + 3CO_2.$$

5. K_2CO_3 or Na_2CO_3 produces the same precipitate, but does not redissolve it when added in excess.

6. On charcoal, before the blowpipe, metallic zinc volatilizes and burns, forming an incrustation of **zinc oxide,** ZnO, which is yellow while hot, but becomes white on cooling. If this coating be moistened with a drop of cobaltous nitrate, and again heated in the outer flame, it becomes green from the admixture with cobalt oxide.

REACTIONS OF SOLUBLE SALTS OF COBALT.

Use a 2-per-cent. solution of cobaltous nitrate, $Co(NO_3)_2 \cdot 6H_2O$.

1. H_2S, in the presence of $NH_4C_2H_3O_2$, produces a black precipitate of **cobaltous sulphide,** CoS, insoluble in $HC_2H_3O_2$ and cold dilute HCl, but soluble in hot HCl or HNO_3.

2. NH_4HS precipitates CoS. The precipitation is promoted by the presence of NH_4Cl.

3. KOH or NaOH produces a blue precipitate of **cobaltous hydrate,** $Co(OH)_2$, insoluble in excess, and becoming pink on boiling or exposure to air.

4. NH_4OH causes a precipitate of $Co(OH)_2$, soluble in excess of the reagent, with the production of a red color. Sugar and some other organic compounds prevent the precipitation by the alkali hydrates.

5. KCN gives a red-brown precipitate of **cobaltous cyanide,** $Co(CN)_2$.

$$Co(NO_3)_2 + 2KCN = Co(CN)_2 + 2KNO_3.$$

The precipitate dissolves in an excess of KCN to produce **cobaltous potassium cyanide,** $Co(CN)_2 \cdot 4KCN$. From this solution $Co(CN)_2$ is again precipitated by HCl. If, however, the solution be boiled with only a few drops of HCl, $Co(CN)_2$

will not be precipitated on the further addition of HCl, on account of the formation of **potassium cobalticyanide,** $K_6Co_2(CN)_{12}$, through the absorption of oxygen from the air.

$$2(Co(CN)_2.4KCN) + O + H_2O = K_6Co_2(CN)_{12} + 2KOH.$$

Experiments with hydrocyanic acid should be performed in a fume-closet in order to avoid inhaling its fumes.

KOH is without action on $K_6Co_2(CN)_{12}$, but it decomposes the corresponding nickel compound, $Ni_3Co_2(CN)_{12}$, with separation of **nickelous hydrate,** $Ni(OH)_2$.

6. The salts of cobalt color the borax bead **blue.**

REACTIONS OF SOLUBLE SALTS OF NICKEL.

Use a 5-per-cent. solution of nickelous sulphate, $NiSO_4.7H_2O$.

1. H_2S in the presence of $NH_4C_2H_3O_2$, forms a black precipitate of **nickelous sulphide,** NiS, insoluble in $HC_2H_3O_2$ and cold dilute HCl, but soluble in hot HCl or HNO_3.

2. NH_4HS precipitates NiS. The precipitation is promoted by the presence of NH_4Cl.

3. KOH or NaOH produces a green precipitate of **nickelous hydrate,** $Ni(OH)_2$, insoluble in excess.

4. NH_4OH gives $Ni(OH)_2$, soluble in excess of the reagent with the production of a blue color. Sugar and some other organic compounds prevent the precipitation by the alkali hydrates.

5. KCN produces a yellowish-green precipitate of **nickelous cyanide,** $Ni(CN)_2$, which dissolves in an excess of the reagent, yielding **nickelous potassium cyanide,** $Ni(CN)_2 2KCN$.

When this solution is acidified with HCl, $Ni(CN)_2$ is reprecipitated, even after having been previously boiled with only a few drops of HCl.

$$Ni(CN)_2 2KCN + 2HCl = Ni(CN)_2 + 2KCl + 2HCN.$$

If, after adding HCl and boiling, KOH be added until the mixture is alkaline, $Ni(OH)_2$ will be precipitated.

$$Ni(CN)_2 + 2KOH = Ni(OH)_2 + 2KCN.$$

6. The salts of nickel color the borax bead **violet** while hot and **reddish-brown** when cold.

CHART FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP III.

<table>
<tr><td colspan="4">Add NH_4OH to the original solution until strongly alkaline, then acidify slightly with $HC_2H_3O_2$, warm, add H_2S until the liquid smells strongly of the reagent, and filter.</td></tr>
<tr><td colspan="3">Precipitate Zn, Co, Ni.
Wash, dissolve in a boiling-hot mixture of 2 parts HCl and 1 part HNO_3, evaporate almost to dryness, add H_2O and then KOH until distinctly alkaline, and filter.</td><td rowspan="3">Filtrate Mn.
Make alkaline with NH_4OH and add H_2S.
Flesh-colored ppt.
Apply Crum's test to the original solution.</td></tr>
<tr><td colspan="2">Precipitate, Co, Ni.
Wash, dissolve in hot HCl, evaporate almost to dryness, add H_2O and then KCN until the ppt. first formed redissolves, boil with a drop or two of HCl for one or two minutes, then add more HCl until the reaction is acid and boil until all odor of HCN disappears, make alkaline with KOH, and filter.</td><td rowspan="2">Filt. Zn.
Add NH_4HS, warm, and allow to stand.
White ppt.</td></tr>
<tr><td>Ppt. Ni.
Green.
Wash well, allow to drain, and test with borax bead.
Reddish-brown color.</td><td>Filtrate Co.
Evaporate to dryness and test with borax bead.
Blue color.</td></tr>
</table>

NOTES ON THE PRECEDING CHART.

1. Time and work may sometimes be saved by carefully noting the color of the precipitate produced by H_2S; for instance, if not black, Co and Ni are evidently absent.

2. The great delicacy of Crum's test for Mn when conducted under proper conditions recommends its invariable application to the original solution as the best means of detecting that element.

3. In evaporating the solution obtained by dissolving the precipitate in HCl and HNO_3 almost to dryness, precaution should be taken that the material is not overheated around the edge of the liquid and thus rendered partly insoluble in water. To obviate any such occurrence the application of heat should be discontinued when the solution has been reduced to some few drops; the dish should then be held in the fingers and rotated in such a manner that the evaporation of the remaining liquid shall be accomplished by the heat of the vessel.

CHART FOR THE DETECTION OF BASES IN SOLUTIONS CONTAINING SOLUBLE SALTS OF ALL FOREGOING ELEMENTS.

<table>
<tr><td colspan="10">Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Add to the original solution NH_4Cl, NH_4OH and NH_4HS, warm * well and filter.</td></tr>
<tr><td colspan="4">**Precipitate Mn, Zn, Co, Ni.**
Wash, dissolve in HCl and HNO_3, evaporate almost to dryness, add H_2O and then NH_4OH until distinctly alkaline, acidify slightly with $HC_2H_3O_2$, warm, add H_2S, and filter.</td><td colspan="6">**† Filtrate Ba, Sr, Ca, Mg, K, Na, Li, NH_4.**
Evaporate to a small bulk or to dryness to remove NH_4HS, if necessary add H_2O, and filter to remove S, then add $(NH_4)_2CO_3$, boil and filter.</td></tr>
<tr><td colspan="3">**Ppt. Zn, Co, Ni.**
Wash, dissolve in HCl and HNO_3, evaporate almost to dryness, add H_2O and then KOH until distinctly alkaline, agitate and filter.</td><td rowspan="4">**Filt. Mn.**
Add NH_4OH until alkaline, and then H_2S. Flesh-colored precipitate. Apply Crum's test to the original solution.</td><td colspan="3">**Ppt. Ba, Sr, Ca.**
Wash, dissolve in $HC_2H_3O_2$, add H_2O and then K_2CrO_4, filter.</td><td colspan="3">**Filt. Mg, K, Na, Li, NH_4.**
Add $(NH_4)_2HPO_4$, agitate and filter.</td></tr>
<tr><td colspan="2">**Ppt. Co, Ni.**
Wash, dissolve in HCl, evaporate almost to dryness, add H_2O, and treat with KCN and HCl, according to chart on page 22, add KOH until alkaline, and filter.</td><td rowspan="3">**Filt. Zn.**
Add NH_4HS, warm, allow to stand. White ppt.</td><td rowspan="3">**Ppt. Ba.**
Yellow.</td><td colspan="2">**Filt. Sr, Ca.**
Add very dilute H_2SO_4, allow to stand for 10 minutes, filter.</td><td rowspan="3">**Ppt. Mg.**
White, crystalline.</td><td colspan="2">**Filt. K, Na, Li, NH_4.**
Add Na_2HPO_4 and NaOH, boil until all NH_3 is expelled, and filter.</td></tr>
<tr><td rowspan="2">**Ppt. Ni.**
Green. Wash well, allow to drain, and test with borax bead. Reddish-brown color.</td><td rowspan="2">**Filtrate Co.**
Evaporate to dryness, and test residue with borax bead. Blue color.</td><td rowspan="2">**Ppt. Sr.**
White. Confirm by flame test. Intense red color.</td><td rowspan="2">**Filt. Ca.**
Add NH_4OH in excess and $(NH_4)_2C_2O_4$. White ppt.</td><td rowspan="2">**Ppt. Li.**
White. Confirm by flame test. Crimson color.</td><td>**Filt. K, Na.**
Acidify with $HC_2H_3O_2$, add $Co_2(NO_2)_6$-$6NaNO_2$. Yellow ppt. indicates K.</td></tr>
<tr><td>Test original solution for Na and NH_4.</td></tr>
</table>

* See Note 1 on following page.

† See Note 2 on following page.

NOTES ON THE PRECEDING CHART.

1. It is particularly important not to filter immediately after adding NH_4HS in the first precipitation, otherwise the Mn will not be thoroughly precipitated.

2. When Ni is present it may remain in solution in the NH_4HS, causing the filtrate to be dark; in which case a dark precipitate of NiS will separate upon evaporating the filtrate in a dish to remove NH_4HS.

The indication of the complete removal of the NH_4HS is a colorless, supernatant liquid, either remaining from the partial evaporation of the filtrate, or obtained by adding H_2O to the residue in the case of evaporation to dryness.

After filtering proceed with the colorless filtrate, while the NiS on the filter is being washed and afterwards dissolved along with the precipitate of Mn, Zn, Co, Ni, and in the same boiling-hot mixture of HCl and HNO_3.

Group IV. Iron, Cerium, Aluminum, Chromium.

REACTIONS OF IRON AS SOLUBLE FERROUS SALTS.

Use a 2-per-cent. solution of ferrous sulphate, $FeSO_4.7H_2O$.

1. $K_4Fe(CN)_6$, in neutral or slightly acid solution, gives a white (rapidly changing to light blue) precipitate of **potassium ferrous ferrocyanide**, $K_2Fe(Fe(CN)_6)$, known as Everett's salt.

$$FeSO_4 + K_4Fe(CN)_6 = K_2Fe(Fe(CN)_6) + K_2SO_4.$$

Alkali hydrates decompose this compound, forming **ferrous hydrate**, $Fe(OH)_2$, and a ferrocyanide of the base used.

$$K_2Fe(Fe(CN)_6) + 2KOH = Fe(OH)_2 + K_4Fe(CN)_6.$$

2. $K_6Fe_2(CN)_{12}$, in neutral or slightly acid solution, forms a dark-blue precipitate of **ferrous ferricyanide**, $Fe_3Fe_2(CN)_{12}$, known as Turnbull's blue.

$$3FeSO_4 + K_6Fe_2(CN)_{12} = Fe_3Fe_2(CN)_{12} + 3K_2SO_4.$$

If the solutions be very dilute there is produced merely a deep blue-green coloration. Alkali hydrates decompose the precipitate.

3. KCNS produces no change in color.

4. H_2S, in acid solution, does not cause a precipitate.

5. NH_4HS, with a neutral or alkaline solution, forms a black precipitate of **ferrous sulphide**, FeS, soluble in HCl or HNO_3. NH_4Cl promotes the formation of this precipitate.

6. KOH or NaOH, or NH_4OH in the absence of NH_4Cl, produces a dirty-green precipitate of **ferrous hydrate**, $Fe(OH)_2$.

This precipitate rapidly becomes reddish-brown, owing to formation of **ferric hydrate,** $Fe_2(OH)_6$, through absorption of oxygen from the air. Non-volatile organic acids and sugar retard the precipitation of $Fe(OH)_2$.

7. K_2CO_3 or Na_2CO_3 causes a white precipitate of **ferrous carbonate,** $FeCO_3$, which rapidly becomes brown, as does $Fe(OH)_2$. This oxidation is retarded by the use of sugar.

REACTIONS OF IRON AS SOLUBLE FERRIC SALTS.

Use a 2-per-cent. solution of ferric chloride, $Fe_2Cl_6 . 12H_2O$.

1. $K_4Fe(CN)_6$, in neutral or slightly acid solution, produces a dark-blue precipitate of **ferric ferrocyanide,** $(Fe_2)_2(Fe(CN)_6)_3$, known as Prussian blue.

$$2Fe_2Cl_6 + 3K_4Fe(CN)_6 = (Fe_2)_2(Fe(CN)_6)_3 + 12KCl.$$

Alkali hydrates decompose the precipitate, forming **ferric hydrate,** $Fe_2(OH)_6$, and a ferrocyanide of the base used.

$$(Fe_2)_2(Fe(CN)_6)_3 + 12KOH = 2Fe_2(OH)_6 + 3K_4Fe(CN)_6.$$

2. $K_6Fe_2(CN)_{12}$ forms no precipitate, but produces a deep **reddish-brown** or **olive-green** color. The olive-green color is due to traces of ferrous salt.

3. KCNS imparts to acid solutions a deep blood-red color, due to the formation of **ferric sulphocyanate,** $Fe_2(CNS)_6$.

$$Fe_2Cl_6 + 6KCNS = Fe_2(CNS)_6 + 6KCl.$$

Dilute solutions show this reaction best.

This color is prevented or immediately destroyed by $HgCl_2$.

4. H_2S produces in acid solution a whitish turbidity, due to separation of sulphur from the reagent, the ferric salt being at the same time reduced to the ferrous condition.

$$2Fe_2Cl_6 + 2H_2S = 4FeCl_2 + 4HCl + S_2.$$

In alkaline solutions this reagent acts as an alkali sulphide.

5. NH_4HS causes a black precipitate of **ferrous sulphide,** FeS, sulphur separating at the same time.

$$2Fe_2Cl_6 + 6NH_4OH + 6NH_4HS = 4FeS + 12NH_4Cl + 6H_2O + S_2.$$

6. KOH, NaOH, or NH_4OH precipitates reddish-brown **ferric hydrate,** $Fe_2(OH)_6$.

Non-volatile organic acids and sugar prevent this precipitation.

7. K_2CO_3 or Na_2CO_3 precipitates $Fe_2(OH)_6$, CO_2 escaping at the same time.

$$Fe_2Cl_6 + 3Na_2CO_3 + 3H_2O = Fe_2(OH)_6 + 6NaCl + 3CO_2.$$

8. With borax in the oxidizing blowpipe flame ferrous and ferric compounds give **dark yellow-colored** beads while hot, and **paler yellow** when cold. In the reducing flame the beads change to **bottle-green.**

REACTIONS OF SOLUBLE SALTS OF CERIUM.

Use a 2-per-cent. solution of cerous chloride, Ce_2Cl_6.

1. NH_4HS causes a white precipitate of **cerous hydrate,** $Ce_2(OH)_6$, H_2S being liberated.

$$Ce_2Cl_6 + 6NH_4HS + 6H_2O = Ce_2(OH)_6 + 6NH_4Cl + 6H_2S.$$

2. KOH, NaOH, or NH_4OH produces the same precipitate of $Ce_2(OH)_6$. $H_3C_6H_5O_7$ prevents this precipitation.

3. $(NH_4)_2C_2O_4$ forms a white precipitate of **cerous oxalate,** $Ce_2(C_2O_4)_3$.

4. Na_2HPO_4 precipitates white **cerous phosphate,** $Ce_2(PO_4)_2$.

$$Ce_2Cl_6 + 2Na_2HPO_4 = Ce_2(PO_4)_2 + 4NaCl + 2HCl.$$

The presence of non-volatile organic acids does not interfere with the formation of this precipitate.

5. With a borax bead before the blowpipe the salts of cerium behave like those of iron.

REACTIONS OF SOLUBLE SALTS OF ALUMINUM.

Use a 2-per-cent. solution of potassium alum, $Al_2K_2(SO_4)_4 \cdot 24H_2O$.

1. NH_4HS produces a white gelatinous precipitate of **aluminum hydrate,** $Al_2(OH)_6$, H_2S being set free.

2. NH_4OH precipitates $Al_2(OH)_6$, which is insoluble in excess of the reagent (an important distinction from zinc). Heat facilitates this precipitation.

3. KOH or NaOH causes a precipitate of $Al_2(OH)_6$, which dissolves in an excess to form an **aluminate** of the base used, as, for instance, $Al_2(OK)_6$. This is not reprecipitated by boiling (a distinction from zinc and chromium); but, when warmed with NH_4Cl, decomposition ensues with precipitation of $Al_2(OH)_6$.

$$Al_2(OK)_6 + 6NH_4Cl = Al_2(OH)_6 + 6NH_3 + 6KCl.$$

4. K_2CO_3 or Na_2CO_3 produces $Al_2(OH)_6$, insoluble in excess, CO_2 escaping at the same time.

The presence of non-volatile organic acids and sugar prevents complete precipitation in the foregoing reactions.

REACTIONS OF SOLUBLE SALTS OF CHROMIUM.

Use a 2 per-cent. solution of chromic chloride, Cr_2Cl_6.

1. NH_4HS produces a greenish precipitate of **chromic hydrate**, $Cr_2(OH)_6$, H_2S being set free.

2. NH_4OH forms the same precipitate of $Cr_2(OH)_6$, insoluble in excess of the reagent.

3. KOH or NaOH causes the precipitation of $Cr_2(OH)_6$, which is soluble in an excess, but reprecipitated on boiling (a distinction from aluminum).

4. K_2CO_3 or Na_2CO_3 precipitates green **basic chromium carbonate.**

5. When a salt of chromium is fused on a platinum foil with a mixture of 1 part KNO_3 and 2 parts K_2CO_3, the mass becomes yellow from the formation of **potassium chromate**, K_2CrO_4.

$$Cr_2Cl_6 + 2KNO_3 + 4K_2CO_3 = 2K_2CrO_4 + N_2O_2 + 6KCl + 4CO_2.$$

The presence of this compound may be proved by dissolving the cooled mass in water, and, after acidifying with acetic acid, adding $AgNO_3$ or $Pb(C_2H_3O_2)_2$, the former of which precipitates red **silver chromate**, Ag_2CrO_4, and the latter yellow **lead chromate**, $PbCrO_4$, if K_2CrO_4 be present.

$$K_2CrO_4 + Pb(C_2H_3O_2)_2 = PbCrO_4 + 2KC_2H_3O_2.$$

If sodium salts be substituted, Na_2CrO_4 will be obtained.

6. With the borax bead in the inner blowpipe flame chromium compounds give a **green** color.

CHART FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP IV.

<table>
<tr><td colspan="4">Evaporate a portion of the original solution to dryness, mix the residue intimately with 2 parts Na_2CO_3 and 1 part KNO_3, and fuse on platinum foil. Boil the cooled mass in a dish with a bulk of water equal to that of the solution evaporated, allow to subside, and decant the liquid upon a filter.</td></tr>
<tr><td colspan="2">Precipitate Fe, Ce.
Wash by decantation, dissolve by heating in the dish with 5 drops H_2SO_4 and 20 drops C_2H_5OH, dilute with water, filter, and divide into two portions.</td><td colspan="2">Filtrate Al, Cr.
Yellow, if Cr be present. Divide into two portions.</td></tr>
<tr><td>Fe.
Add $K_4Fe(CN)_6$. Blue ppt. Test original solution with $K_4Fe(CN)_6$ and $K_6Fe_2(CN)_{12}$ for Fe(ic) and Fe(ous).</td><td>Ce.
Add $H_3C_6H_5O_7$, NH_4OH in excess, and Na_2HPO_4. White ppt.</td><td>Al.
Add NH_4Cl, warm, and allow to stand. White, gelatinous ppt.</td><td>Cr.
Acidify with $HC_2H_3O_2$ and add $Pb(C_2H_3O_2)_2$. Yellow ppt.</td></tr>
</table>

IART FOR THE DETECTION OF BASES IN SOLUTIONS CONTAINING SOLUBLE SALTS OF ALL FOREGOING ELEMENTS.

<table>
<tr><td colspan="14">Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Add to the original solution NH_4Cl, NH_4OH, NH_4HS, warm well and filter.</td></tr>
<tr><td colspan="8">**Precipitate Fe, Ce, Al, Cr, Mn, Zn, Co, Ni.***
Wash, dissolve in a boiling-hot mixture of 2 parts HCl and 1 part HNO_3, evaporate almost to dryness, add H_2O and then NH_4OH in excess, agitate and filter.</td><td colspan="6">**Filtrate Ba, Sr, Ca, Mg, K, Na, Li, NH_4.**
(If Ni is suspected proceed by note on page 836.)
Evaporate to remove NH_4HS, add $(NH_4)_2CO_3$, boil, filter.</td></tr>
<tr><td colspan="4">**Ppt. Fe, Ce, Al, Cr.**
Wash, allow to drain, mix with 2 parts Na_2CO_3 and 1 part KNO_3, fuse on platinum foil, allow to cool, boil with H_2O, and decant the liquid upon a filter.</td><td colspan="4">**Filt. Mn, Zn, Co, Ni.**
Acidify slightly with $HC_2H_3O_2$, warm, add H_2S, and filter.</td><td colspan="3">**Ppt. Ba, Sr, Ca.**
Wash, dissolve in $HC_2H_3O_2$, dilute, add K_2CrO_4, and filter.</td><td colspan="3">**Filt. Mg, K, Na, Li, NH_4.**
Add $(NH_4)_2HPO_4$, agitate, and filter.</td></tr>
<tr><td colspan="2">**Ppt. Fe, Ce.†**
Wash by decantation, dissolve by heating in the dish with 5 drops H_2SO_4 and 20 drops C_2H_5OH, dilute with H_2O, filter, and divide into two portions.</td><td colspan="2">**Filt. Al, Cr.**
Yellow, if Cr be present. Divide into two portions.</td><td colspan="3">**Ppt. Zn, Co, Ni.**
Wash, dissolve in boiling-hot HCl and HNO_3, evaporate almost to dryness, add H_2O and then KOH until alkaline, agitate, and filter.</td><td rowspan="3">**Filt. Mn.**
Add NH_4OH until alkaline and H_2S. Flesh-colored ppt. Apply Crum's test to original solution.</td><td rowspan="3">**Ppt. Ba.**
Yellow.</td><td colspan="2">**Filt. Sr, Ca.**
Add very dilute H_2SO_4, allow to stand for 10 minutes, filter.</td><td rowspan="3">**Ppt. Mg.**
White, crystalline.</td><td colspan="2">**Filt. K, Na, Li, NH_4.**
Add Na_2HPO_4 and NaOH, boil until all NH_3 is expelled, and filter.</td></tr>
<tr><td rowspan="2">**Fe.**
Add $K_4Fe(CN)_6$. Blue ppt. Test original solution for Fe(ous) and Fe(ic).</td><td rowspan="2">**Ce.**
Add $H_3C_6H_5O_7$, NH_4OH in excess, and Na_2HPO_4. White ppt.</td><td rowspan="2">**Al.**
Add NH_4Cl, warm well, and allow to stand. White, gelatinous ppt.</td><td rowspan="2">**Cr.**
Acidify with $HC_2H_3O_2$, and add $Pb(\bar{A})_2$. Yellow ppt.</td><td colspan="2">**Ppt. Co, Ni.**
Wash, dissolve in hot HCl. Evaporate almost to dryness, add H_2O and treat with KCN and HCl, according to chart, page 834, add KOH until alkaline, filter.</td><td rowspan="2">**Filt. Zn.**
Add NH_4HS, warm, allow to stand. White ppt.</td><td rowspan="2">**Ppt. Sr.**
White. Confirm by flame test.</td><td rowspan="2">**Filt. Ca.**
Add NH_4OH in excess and $(NH_4)_2C_2O_4$. White ppt.</td><td rowspan="2">**Ppt. Li.**
White. Confirm by flame test.</td><td>**Filt. K, Na.**
Acidify with $HC_2H_3O_2$, add $Co_2(NO_2)_6 6NaNO_2$. Yellow ppt. indicates K.</td></tr>
<tr><td>**Ppt. Ni.**
Green. Confirm by borax bead.</td><td>**Filt. Co.**
Evaporate to dryness and test with borax bead.</td><td>Test original solution for Na and NH_4.</td></tr>
</table>

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* See notes on following page.

† Mn is sometimes found in this precipitate; hence the necessity of always applying Crum's test to the original solution.

NOTES ON THE PRECEDING CHART.

1. When the first precipitate is dissolved in HCl and HNO_3, the Fe must be completely oxidized by boiling with the HNO_3, so its precipitation as $Fe_2(OH)_6$ by the NH_4OH shall be complete.

2. When phosphoric acid is present the members of Group II. precipitate with those of Group IV., and require an entirely different method of separation. It is desirable, however, for the student first to familiarize himself with the simpler soluble salts, and undertake the more difficult cases of salts insoluble in water only after the acids have been considered. (See page 66.)

Group V. Arsenic, Antimony, Tin, Gold, Platinum.

REACTIONS OF SOLUBLE ARSENOUS COMPOUNDS.

Use a 1-per-cent. solution of arsenous oxide, As_2O_3.

1. H_2S produces a yellow color, but no precipitate, until HCl is added, when a yellow precipitate of **arsenous sulphide**, As_2S_3, falls.

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

This precipitate is insoluble in boiling HCl, but soluble in NH_4HS, $(NH_4)_2S$, NH_4OH, or $(NH_4)_2CO_3$, from which it is reprecipitated by acidifying with HCl.

2. NH_4HS causes the formation of As_2S_3, which remains in solution as **ammonium sulpharsenite**, $(NH_4)_3AsS_3$.

$$As_2O_3 + 6NH_4HS = 2(NH_4)_3AsS_3 + 3H_2O.$$

On the addition of HCl, As_2S_3 is precipitated.

$$2(NH_4)_3AsS_3 + 6HCl = As_2S_3 + 6NH_4Cl + 3H_2S.$$

3. $AgNO_3$ produces no precipitate until a few drops of dilute NH_4OH are added, when a yellow precipitate of **silver arsenite**, Ag_3AsO_3, falls.

$$As_2O_3 + 6AgNO_3 + 6NH_4OH = 2Ag_3AsO_3 + 6NH_4NO_3 + 3H_2O.$$

The precipitate is soluble in an excess of NH_4OH, and in HNO_3.

4. $CuSO_4$, under similar circumstances, produces a yellowish-green precipitate of **cupric arsenite**, $CuHAsO_3$.

$$As_2O_3 + 2CuSO_4 + 4NH_4OH = 2CuHAsO_3 + 2(NH_4)_2SO_4 + H_2O.$$

The precipitate is soluble in an excess of NH_4OH, and in HNO_3.

REACTIONS OF SOLUBLE ARSENIC COMPOUNDS.

Use a 1-per-cent. solution of sodium arsenate, $Na_2HAsO_4 \cdot 7H_2O$.

1. H_2S causes, in acid solution only, a yellow precipitate of **arsenous sulphide,** As_2S_3, mixed with sulphur.

$$2Na_2HAsO_4 + 5H_2S + 4HCl = As_2S_3 + S_2 + 4NaCl + 8H_2O.$$

This reaction takes place slowly, but is accelerated by heat.

2. NH_4HS produces no precipitate, but forms **arsenic sulphide,** As_2S_5, which remains in solution as **ammonium sulpharsenate,** $(NH_4)_3AsS_4$.

$$Na_2HAsO_4 + 5NH_4HS = (NH_4)_3AsS_4 + Na_2S + 2NH_3 + 4H_2O.$$

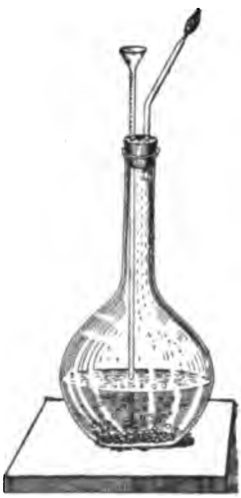
Upon the addition of HCl, As_2S_5 is precipitated, and not As_2S_3 and S.

$$2(NH_4)_3AsS_4 + 6HCl = As_2S_5 + 6NH_4Cl + 3H_2S.$$

3. $AgNO_3$ with a small amount of NH_4OH produces a chocolate-colored precipitate of **silver arsenate,** Ag_3AsO_4, soluble in excess of NH_4OH and in HNO_3.

4. $CuSO_4$, under similar circumstances, forms a bluish-green precipitate of **cupric arsenate,** $CuHAsO_4$.

FIG. 5.



Marsh's test.

The following tests are applicable to both arsenous and arsenic compounds :

1. **Marsh's Test.**—Generate hydrogen in the usual way, allowing it to escape through a glass tube drawn out at the end so as to form a small orifice (Fig. 5).

In very exact cases, the gas should be dried by passing over anhydrous calcium chloride. When all the air has been expelled (which should be determined by collecting a small test-tube full and holding its mouth to a flame ; if the gas burn quietly, without explosion, it is pure), ignite the escaping gas. It should burn with a colorless or yellow flame,—in the latter case the color is due to the sodium in the glass. To make sure that the zinc and sulphuric acid are free from arsenic, a crucible-lid or capsule is pressed into the inner flame of the burning hydrogen, when, in the absence of arsenic, there will be no deposit on the white surface. When the purity of the materials has thus been established, add, through the funnel-tube, a solution of some soluble compound of arsenic, and wash it down with a little water. The flame will become of a pale-blue color, due to the combustion of the **hydrogen arsenide**, H_3As, produced by the union of the nascent hydrogen with the arsenic.

$$Na_2HAsO_4 + 4H_2 = H_3As + 2NaOH + 2H_2O.$$

Upon again bringing the cold porcelain into the flame, a blackish-brown stain possessing a decided metallic lustre will form on it. This deposit is readily soluble in NaOCl or $Ca(OCl)_2$.

2. **Gutzeit's Test.**—Generate hydrogen in a test-tube from zinc and dilute sulphuric acid, prepared by adding a small quantity of strong sulphuric acid to thirty times its volume of water. Hold over the mouth of the tube, first, a piece of filter paper moistened with a drop of solution of lead acetate to detect H_2S, and, afterwards, another piece moistened with a drop of solution of silver nitrate. If the zinc and sulphuric acid are pure no discoloration of the moistened spot on either paper will occur. Now add some soluble compound of arsenic, and place over the mouth of the test-tube a filter paper which has been previously moistened with silver nitrate solution and dried. The presence of arsenic is indicated by the formation of a bright yellow stain, due to a compound of **silver arsenide**, Ag_3As, with **silver nitrate**, $AgNO_3$.

$$6AgNO_3 + H_3As = (AgNO_3)_3.Ag_3As + 3HNO_3.$$

Upon the application of water the stain changes to black or brown from the separation of metallic **silver**, Ag.

$$(AgNO_3)_3.Ag_3As + 3H_2O = 3Ag_2 + 3HNO_3 + H_3AsO_3.$$

3. **Reinsch's Test.**—Boil some strips of copper with dilute HCl; if no discoloration of the copper takes place the solution of the arsenic compound may be added. **Arsenic**, As, is precipitated, the copper immediately becoming coated with an iron-gray metallic film of **copper arsenide**, Cu_5As_2.

$$As_2O_3 + 3Cu + 6HCl = As_2 + 3CuCl_2 + 3H_2O.$$

Pour off the liquid, dry the strips by holding them in the flame of a Bunsen burner with the fingers so they do not become too hot; then place them in a clean, dry, narrow test-tube and heat gently, when a white ring of **arsenous oxide,** As_2O_3, will form on the tube above the copper, and is readily distinguished by the characteristic octohedral shape of the crystals composing it.

$$Cu_5As_2 + 4O_2 \text{ (from the air)} = As_2O_3 + 5CuO.$$

4. **Fleitmann's Test.**—Generate hydrogen in a test-tube from zinc and solution of potassium hydrate; moisten a piece of filter paper with one drop of solution of silver nitrate, place it over the mouth of the tube and heat the mixture,—there should be no coloration of the moistened spot on the paper if the reagents are free from arsenic. Now add some soluble compound of arsenic, and the silver nitrate will immediately become black, owing to the liberation of metallic **silver,** Ag.

$$H_3As + 6AgNO_3 + 3H_2O = 3(Ag_2) + H_3AsO_3 + 6HNO_3.$$

Gatehouse's modification of this test consists in employing aluminum wire cut into small pieces instead of zinc. The method of application and results are the same.

5. **Bettendorff's Test.**—To some boiling hydrochloric acid add granulated tin or tin-foil until no more is dissolved. Pour off the liquid and mix it with an equal volume of hydrochloric acid. Boil again; if no coloration or precipitate forms the materials are free from arsenic. Should this be the case, add a relatively small quantity of a solution containing a compound of arsenic and continue to heat. A brown color or precipitate of metallic **arsenic,** As, with a small amount of tin results.

$$As_2O_3 + 6HCl + 3SnCl_2 = As_2 + 3SnCl_4 + 3H_2O.$$

6. Before the blowpipe, on charcoal, arsenic is volatilized, with the characteristic odor of garlic.

REACTIONS OF SOLUBLE ANTIMONY COMPOUNDS.

Use a 1-per-cent. solution of tartar emetic, $(K(SbO)C_4H_4O_6)_2 \cdot H_2O$.

1. H_2S forms, in solutions acidified with HCl, an orange-colored precipitate of **antimonous sulphide,** Sb_2S_3, soluble in NH_4HS, $(NH_4)_2S$, or boiling HCl, but insoluble in $(NH_4)_2CO_3$.

2. NH_4HS produces a precipitate of Sb_2S_3, readily soluble in excess with the formation of **ammonium sulphantimonite,** $(NH_4)_3SbS_3$, from which HCl again precipitates Sb_2S_3.

3. KOH or NaOH precipitates white **antimonous hydrate,** $Sb(OH)_3$, soluble in an excess of the reagent.

4. NH_4OH precipitates $Sb(OH)_3$, insoluble in an excess of the reagent.

5. Marsh's Test, applied as with arsenic, gives a sooty-black spot of metallic **antimony,** Sb, which is insoluble in NaOCl or $Ca(OCl)_2$, but soluble in NH_4HS.

6. Gutzeit's Test gives at once a black or brown stain of **silver antimonide,** Ag_3Sb.

$$3AgNO_3 + H_3Sb = Ag_3Sb + 3HNO_3.$$

7. Reinsch's Test causes a deposit of Sb on the copper, as with arsenic, but when heated in a tube there is formed a white, amorphous ring of **antimonous oxide,** Sb_2O_3, which is readily distinguished from the crystalline one obtained in the reaction of arsenic.

8. Fleitmann's Test gives no result with antimony compounds, because **hydrogen antimonide,** H_3Sb, is decomposed by alkali hydrates.

9. Bettendorff's Test shows no reaction with antimony, as $SnCl_2$ does not precipitate Sb.

10. Zn and Pt (foil), when warmed with a solution of an antimony compound acidified with HCl, cause a deposition of finely-divided, black metallic Sb upon the Pt, H_3Sb being at the same time evolved.

$$3SbCl_3 + 6H_2 = Sb_2 + 9HCl + H_3Sb.$$

If the foil be warmed in a dish with a few drops of dilute HNO_3, the black Sb will be converted into white Sb_2O_3, soluble in $H_2C_4H_4O_6$.

$$Sb_2 + 2HNO_3 = Sb_2O_3 + H_2O + N_2O_3.$$

11. On charcoal, with Na_2CO_3, before the blowpipe, antimony compounds yield a metallic globule of Sb, while characteristic fumes of white Sb_2O_3 are given off.

REACTIONS OF TIN AS SOLUBLE STANNOUS SALTS.

Use a 2-per-cent. solution of stannous chloride, $SnCl_2.2H_2O$.

1. H_2S precipitates dark-brown **stannous sulphide,** SnS, soluble in boiling HCl or in $(NH_4)_2S$, but insoluble in NH_4HS.

2. KOH or NaOH precipitates white **stannous hydrate,** $Sn(OH)_2$, soluble in an excess of the reagent. On boiling this solution **stannous oxide,** SnO, is precipitated.

$$Sn(OK)_2 + H_2O = SnO + 2KOH.$$

3. NH_4OH precipitates $Sn(OH)_2$, insoluble in an excess of the reagent.

4. $HgCl_2$ causes a white precipitate of **mercurous chloride**, Hg_2Cl_2, the $SnCl_2$ being converted into $SnCl_4$.

$$SnCl_2 + 2HgCl_2 = Hg_2Cl_2 + SnCl_4.$$

This precipitate is blackened by the addition of NH_4OH.

Reactions of Tin as Soluble Stannic Salts.

Use a 2-per-cent. solution of stannic chloride, $SnCl_4.5H_2O$.

1. H_2S produces a yellow precipitate of **stannic sulphide**, SnS_2, soluble in boiling HCl, NH_4HS, or $(NH_4)_2S$.

2. KOH or NaOH precipitates white **stannic acid**, H_2SnO_3.

$$SnCl_4 + 4KOH = H_2SnO_3 + 4KCl + H_2O.$$

The precipitate is soluble in an excess of the reagent; on boiling, no precipitation takes place (distinction from stannous salts).

$$H_2SnO_3 + 2KOH = K_2SnO_3 + 2H_2O.$$

3. NH_4OH produces a precipitate of H_2SnO_3, insoluble in an excess of the reagent.

4. Heated on charcoal, before the blowpipe, with Na_2CO_3 and KCN, metallic **tin**, Sn, is formed from both Sn(ous) and Sn(ic) compounds, with the production of a white incrustation of **stannic oxide**, SnO_2.

5. Zn and Pt (foil), warmed with a solution of a salt of tin acidified with HCl, effects the separation of the Sn as a soft, metallic sediment, soluble in hot HCl.

$$2SnCl_2 + 2H_2 = Sn_2 + 4HCl.$$

Reactions of Soluble Salts of Gold.

Use a 0.5-per-cent. solution of auric chloride, $AuCl_3$.

1. H_2S precipitates black **auric sulphide**, Au_2S_3, insoluble in boiling HCl, NH_4HS, or $(NH_4)_2CO_3$, but soluble in $(NH_4)_2S$ or a mixture of HCl and HNO_3.

2. $H_2C_2O_4$ or $FeSO_4$ precipitates **metallic gold**, Au, as a finely-divided brown powder.

$$2AuCl_3 + 3H_2C_2O_4 = Au_2 + 6HCl + 6CO_2.$$
$$2AuCl_3 + 6FeSO_4 + 3H_2SO_4 = Au_2 + 3Fe_2 3SO_4 + 6HCl.$$

3. $SnCl_2$ mixed with $SnCl_4$ and $FeCl_2$ (prepared by adding Fe_2Cl_6 to $SnCl_2$) produces a purple-red precipitate or coloration

(Purple of Cassius), consisting of the **mixed oxides of gold and tin.**

4. Heated on charcoal, before the blowpipe, salts of gold yield metallic Au.

REACTIONS OF SOLUBLE SALTS OF PLATINUM.

Use a 2-per-cent. solution of platinic chloride, $PtCl_4.5H_2O$.*

1. H_2S causes a brown precipitate of **platinic sulphide,** PtS_2, insoluble in boiling HCl, NH_4HS, or $(NH_4)_2CO_3$, but soluble in $(NH_4)_2S$ or a mixture of HCl and HNO_3.

2. KCl produces a yellow, crystalline precipitate of **potassium platinic chloride,** K_2PtCl_6. The presence of alcohol facilitates the precipitation in this and the next test.

3. NH_4Cl forms a similar precipitate of **ammonium platinic chloride,** $(NH_4)_2PtCl_6$.

4. Fe or Zn precipitates finely-divided black metallic **platinum,** Pt.

5. Heated on charcoal, before the blowpipe, compounds of platinum yield metallic Pt.

CHART FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP V.

<table>
<tr><td colspan="4">Acidify the original solution with HCl, warm, and add H_2S.† Filter (disregard the filtrate after making sure that the precipitation has been complete), transfer the precipitate to a dish, boil with strong HCl, and filter.</td></tr>
<tr><td colspan="3">Precipitate As, Au, Pt.
If yellow, As only is present; if dark, wash, digest with $(NH_4)_2CO_3$, and filter.</td><td rowspan="3">Filtrate Sb, Sn.
Dilute with H_2O, boil in a dish with a piece of platinum foil and a small fragment of zinc, so the metals touch. The platinum will be coated with black, metallic Sb, while the Sn will be deposited as a metallic sediment. This sediment is dissolved in HCl and tested with $HgCl_2$, which produces a white precipitate if Sn be present. Warm the foil with a few drops of HNO_3 in a dish until the black color disappears, rinse with solution of $H_2C_4H_4O_6$, pour into a test-tube and add H_2S; orange-colored precipitate if Sb be present.</td></tr>
<tr><td colspan="2">Precipitate Au, Pt.
Dissolve in 2 parts HCl and 1 part HNO_3. Divide into two portions.</td><td rowspan="2">Filt. As.
Acidify with HCl. Yellow ppt.</td></tr>
<tr><td>Au.
Apply Purple of Cassius test to this and also to original solution.</td><td>Pt.
Add KCl. Yellow ppt. Confirm by testing original solution.</td></tr>
</table>

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* Or chloroplatinic acid, $H_2PtCl_6.6H_2O$.

† See notes on following page.

Notes on the Preceding Chart.

1. In the application of H_2S the solution to be tested should always be well warmed and very thoroughly saturated with the reagent, otherwise the precipitation of As, when present in the arsenic state, will not be complete.

2. To transfer a precipitate to a dish use is made of the wash-bottle, the jet from which is directed against the moist precipitate on the unfolded filter in such a way that the least possible quantity of water may be used. After settling, the greater part of the water should be decanted from the precipitate, which should then be treated with the next reagent.

3. If stannic salts are known to be absent, and the precipitate produced by H_2S is yellow, As only is present; if orange-colored, Sb is present, and As may be. Under such circumstances, the readiest method of separation is to wash the precipitate and then treat it with $(NH_4)_2CO_3$; As will be dissolved, and may be detected in the filtrate by acidifying with HCl, while Sb remains on the filter.

CHART FOR THE DETECTION OF BASES IN SOLUTIONS CONTAINING SOLUBLE SALTS OF ALL FOREGOING ELEMENTS.

<table>
<tr><td colspan="15">As, Sb, Sn, Au, Pt, Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Acidify the original solution with HCl, then add H_2S until, after warming, the mixture smells strongly of the reagent, and filter.</td></tr>
<tr><td colspan="2">Ppt. As, Sb, Sn, Au, Pt.
Wash, boil with strong HCl, and filter.</td><td colspan="13">Filt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Add NH_4Cl, NH_4OH, NH_4HS, warm well, and filter.</td></tr>
<tr><td rowspan="5">Ppt. As, Au, Pt.
Separate according to chart, p. 35.</td><td rowspan="5">Filt. Sb, Sn.
Separate according to chart, p. 35.</td><td colspan="7">Ppt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni.
Wash, dissolve in 2 parts HCl and 1 part HNO_3, evaporate almost to dryness, add H_2O and then NH_4OH in excess, and filter.</td><td colspan="6">Filt. Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Evaporate to remove NH_4HS, add $(NH_4)_2CO_3$, boil, filter.</td></tr>
<tr><td colspan="3">Ppt. Fe, Ce, Al, Cr.
Wash, allow to drain, fuse on foil with Na_2CO_3 and KNO_3, boil cooled mass with H_2O, decant upon a filter.</td><td colspan="4">Filt. Mn, Zn, Co, Ni.
Acidify slightly with $HC_2H_3O_2$, add H_2S, filter.</td><td colspan="3">Ppt. Ba, Sr, Ca.
Wash, dissolve in $HC_2H_3O_2$, dilute, add K_2CrO_4, filter.</td><td colspan="3">Filt. Mg, K, Na, Li, NH_4.
Add $(NH_4)_2HPO_4$, agitate, filter.</td></tr>
<tr><td rowspan="3">Ppt. Fe, Ce.
Separate according to chart, p. 27.</td><td colspan="2">Filt. Al, Cr.
Yellow, if Cr be present. Divide into two portions.</td><td colspan="3">Ppt. Zn, Co, Ni.
Wash, dissolve in 2 parts HCl and 1 part HNO_3, evaporate almost to dryness, add H_2O and then KOH until distinctly alkaline, filter.</td><td rowspan="3">Filt. Mn.
Add NH_4OH in excess and H_2S. Flesh-colored ppt. Apply Crum's test to original solution.</td><td rowspan="3">Ppt. Ba.
Yellow.</td><td colspan="2">Filt. Sr, Ca.
Add very dilute H_2SO_4, allow to stand, filter.</td><td rowspan="3">Ppt. Mg.
White, crystalline.</td><td colspan="2">Filt. K, Na, Li, NH_4.
Add Na_2HPO_4 and NaOH, boil until all NH_3 is expelled, and filter.</td></tr>
<tr><td rowspan="2">Al.
Add NH_4Cl, warm well, and allow to stand. White, gelatinous ppt.</td><td rowspan="2">Cr.
Acidify with $HC_2H_3O_2$ and add $Pb(\bar{A})_2$. Yellow ppt.</td><td colspan="2">Ppt. Co, Ni.
Wash, dissolve in HCl, evaporate almost to dryness, add H_2O, and treat with KCN and HCl according to chart, p. 22, then add KOH until alkaline, filter.</td><td rowspan="2">Filt. Zn.
Add NH_4HS, warm, allow to stand. White ppt.</td><td rowspan="2">Ppt. Sr.
White. Confirm by flame test.</td><td rowspan="2">Filt. Ca.
Add NH_4OH in excess and $(NH_4)_2C_2O_4$. White ppt.</td><td rowspan="2">Ppt. Li.
White. Confirm by flame test.</td><td>Filt. K, Na.
Acidify with $HC_2H_3O_2$, add $Co_2(NO_2)_6\cdot 6NaNO_2$. Yellow ppt. indicates K.</td></tr>
<tr><td>Ppt. Ni.
Green. Confirm by borax bead.</td><td>Filt. Co.
Evaporate to dryness and test with borax bead.</td><td>Test original solution for Na and NH_4.</td></tr>
</table>

Group VI. Mercury(ic), Bismuth, Copper, Cadmium.

REACTIONS OF SOLUBLE MERCURIC SALTS.

Use a 2-per-cent. solution of mercuric chloride, $HgCl_2$.

1. H_2S or NH_4HS produces, when in small proportion, a whitish precipitate of $(HgS)_2HgCl_2$; a further addition of the reagent, together with the application of heat, causes the formation of a black precipitate of **mercuric sulphide,** HgS, insoluble in either HCl or HNO_3, but soluble in a mixture of the two. It is insoluble also in NH_4HS or $(NH_4)_2S$.

2. KOH or NaOH produces a yellow precipitate of **mercuric oxide,** HgO.

$$HgCl_2 + 2KOH = HgO + 2KCl + H_2O.$$

Unless the reagent be in excess a brown precipitate of a basic salt is formed.

3. NH_4OH precipitates white **mercuric ammonium chloride,** NH_2HgCl.

$$HgCl_2 + 2NH_4OH = NH_2HgCl + NH_4Cl + 2H_2O.$$

This precipitate is readily soluble in HCl or $HC_2H_3O_2$.

4. K_2CrO_4 produces a red precipitate of **mercuric chromate,** $HgCrO_4$.

5. KI precipitates **mercuric iodide,** HgI_2, at first yellow, but rapidly becoming scarlet.

$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$

This precipitate is readily soluble in excess of KI or $HgCl_2$.

6. $SnCl_2$, in small quantity, in the presence of HCl, precipitates white **mercurous chloride,** Hg_2Cl_2. On the addition of a larger quantity of the reagent, Hg_2Cl_2 is reduced to gray metallic **mercury,** Hg, which may be collected into a globule.

$$Hg_2Cl_2 + SnCl_2 = Hg_2 + SnCl_4.$$

7. Na_2CO_3 produces a reddish-brown precipitate of **basic mercuric carbonate,** $HgCO_3(HgO)_3$.

8. Copper turnings boiled with the solution, acidified with HCl, become quickly coated with metallic **mercury,** Hg.

$$2HgCl_2 + Cu_2 = Hg_2 + 2CuCl_2.$$

The presence of HNO_3 must be avoided or the copper will be dissolved; when present in the material to be tested, it should be expelled by evaporating the solution with HCl to dryness. If the coated turnings are carefully dried at a low temperature, placed in the bottom of a dry, narrow test-tube and heated, a ring composed of minute globules of Hg will form on the cool part of the tube. These globules may be formed into larger ones by pressing them together with a glass rod, until they may be seen with the naked eye. Instead of distilling the Hg from the copper turnings in the foregoing manner, the smooth surfaces of the latter may be rubbed with filter paper, whereupon they will acquire a silvery lustre due to the mercury.

9. Before the blowpipe, HgO breaks up into Hg and O. HgS, under similar circumstances, sublimes unchanged.

REACTIONS OF SOLUBLE SALTS OF BISMUTH.

Use a 2-per-cent. solution of bismuth nitrate, $Bi(NO_3)_3.5H_2O$.

1. H_2S or NH_4HS produces a black precipitate of **bismuth trisulphide,** Bi_2S_3, insoluble in NH_4HS or $(NH_4)_2S$, but soluble in boiling HNO_3.

2. KOH, NaOH, or NH_4OH forms a white precipitate of **bismuth hydrate,** $Bi(OH)_3$, converted, through loss of H_2O by boiling, into yellow **bismuth oxide,** Bi_2O_3.

$$2Bi(OH)_3 = Bi_2O_3 + 3H_2O.$$

Both the hydrate and oxide dissolve in HCl to form **bismuth chloride,** $BiCl_3$.

3. K_2CrO_4 precipitates yellow **bismuth chromate,** $Bi_2(CrO_4)_3$.

4. KI forms a brown precipitate of **bismuth iodide,** BiI_3, soluble in excess of the reagent.

5. H_2O in considerable quantity, when there is not an excess of free acid, precipitates white **bismuth subnitrate,** $BiONO_3.H_2O$.

$$Bi(NO_3)_3 + 2H_2O = BiONO_3.H_2O + 2HNO_3.$$

When bismuth chloride is so diluted, white **bismuth oxychloride,** BiOCl, is produced.

6. Na_2CO_3 precipitates white **bismuth subcarbonate,** $(BiO)_2CO_3.H_2O$.

$$2Bi(NO_3)_3 + 3Na_2CO_3 + H_2O = (BiO)_2CO_3.H_2O + 6NaNO_3 + 2CO_2.$$

7. Bismuth salts on charcoal, before the blowpipe, yield a hard bead of **bismuth,** Bi, and a characteristic incrustation of **bismuth oxide,** Bi_2O_3, deep orange-yellow while hot, but pale yellow when cold.

REACTIONS OF SOLUBLE SALTS OF COPPER.

Use a 2-per-cent. solution of cupric sulphate, $CuSO_4.5H_2O$.

1. H_2S or NH_4HS precipitates black **cupric sulphide,** CuS, slightly soluble in $(NH_4)_2S$ and NH_4HS, but readily dissolved by KCN or boiling HNO_3.

2. KOH or $NaOH$ produces a light-blue precipitate of **cupric hydrate,** $Cu(OH)_2$, insoluble in excess of the reagent.

In the presence of non-volatile organic acids this precipitation does not take place, but a blue color results.

Boiling converts the $Cu(OH)_2$, through loss of H_2O, into black **cupric oxyhydrate,** $(CuO)_2Cu(OH)_2$.

$$3Cu(OH)_2 = (CuO)_2Cu(OH)_2 + 2H_2O.$$

3. NH_4OH in small quantity forms a greenish-purple precipitate, readily soluble in an excess of the reagent, forming **tetra-ammonio-cupric sulphate,** $(NH_3)_4CuSO_4.H_2O$, which imparts to the solution an azure-blue color.

$$CuSO_4 + 4NH_4OH = (NH_3)_4CuSO_4.H_2O + 3H_2O.$$

4. $K_4Fe(CN)_6$ precipitates reddish-brown **cupric ferrocyanide,** $Cu_2Fe(CN)_6$.

5. Metallic Fe or Zn precipitates red metallic **copper,** Cu, which collects on the Fe or Zn.

6. In the outer blowpipe flame copper salts color the borax bead **green** while hot, and **blue** when cold. In the inner flame, after moistening with $SnCl_2$, the bead becomes **red,** owing to the formation of **cuprous oxide,** Cu_2O.

REACTIONS OF SOLUBLE SALTS OF CADMIUM.

Use a 2-per-cent. solution of cadmium nitrate, $Cd(NO_3)_2.4H_2O$.

1. H_2S or NH_4HS precipitates yellow **cadmium sulphide,** CdS, insoluble in $(NH_4)_2S$, NH_4HS, or KCN, but soluble in hot HNO_3 or dilute H_2SO_4.

2. KOH or $NaOH$ produces a white precipitate of **cadmium hydrate,** $Cd(OH)_2$, insoluble in excess of the reagent.

3. NH_4OH causes the precipitation of $Cd(OH)_2$, which dissolves in an excess of the reagent.

4. Na_2CO_3 produces a white precipitate of **cadmium oxycarbonate,** insoluble in excess, but slightly soluble in ammonium salts, and readily soluble in NH_4OH.

5. On charcoal, before the blowpipe, the salts of cadmium are

reduced to **cadmium**, Cd, and volatilize, forming a brownish incrustation of **cadmium oxide**, CdO.

CHART FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP VI.

<table>
<tr><td colspan="4">Warm the original solution and completely precipitate it with H_2S, filter (disregard the filtrate), wash the ppt., transfer it to a dish, boil with HNO_3 (sp. gr. 1.20), and filter.</td></tr>
<tr><td rowspan="3">Ppt. Hg(ic).
Black.
Confirm by note 2.</td><td colspan="3">Filtrate Bi, Cu, Cd.
Add NH_4OH in excess and filter.</td></tr>
<tr><td rowspan="2">Ppt. Bi.
White.
Confirm by note 3.</td><td colspan="2">Filtrate Cu, Cd.
Blue, if Cu be present. Add H_2S. If the ppt. be yellow, Cd only is present; if dark, filter (disregard the filtrate), wash the ppt., transfer it to a dish, boil with 1 part H_2SO_4 and 10 parts H_2O, and filter.</td></tr>
<tr><td>Ppt. Cu.
Black.</td><td>Filtrate Cd.
Dilute with H_2O and add H_2S.
Yellow ppt.</td></tr>
</table>

NOTES ON THE PRECEDING CHART.

1. Unless excess of H_2S be used, and the solution warmed, Hg will not be thoroughly precipitated.

2. The precipitate of HgS left undissolved upon boiling with HNO_3 is heavy, sinks to the bottom of the dish, and should be black. Upon long boiling, however, it gradually becomes yellow. Sulphur from the sulphides of the bases dissolved by the HNO_3 may be either yellow or black, but is readily distinguished from HgS, because it floats on the liquid. To confirm the presence of Hg, dissolve the precipitate in a mixture of 2 parts HCl and 1 part HNO_3, evaporate carefully to dryness, add H_2O, 2 or 3 drops of HCl, and copper turnings, which, if Hg is present, become coated with globules of that metal.

3. To confirm the presence of Bi, wash the precipitate produced by NH_4OH, treat it with 1 or 2 drops of HCl, and, if necessary, after standing, a few drops of water to displace the liquid from the filter, and allow the solution thus formed to run into a test-tube of water. If Bi is present a white turbidity, due to BiOCl, will result.

Chart for the Detection of Bases in Solutions containing Soluble Salts of all Foregoing Elements.

<table>
<tr><td colspan="19">Hg(ic), Bi, Cu, Cd, As, Sb, Sn, Au, Pt, Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Acidify the original solution with HCl, then add H_2S until, after warming, the mixture smells strongly of the reagent, and filter.</td></tr>
<tr><td colspan="6">Ppt. Hg, Bi, Cu, Cd, As, Sb, Sn, Au, Pt.
Wash, digest with $(NH_4)_2S$,* filter.</td><td colspan="13">Filt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Add NH_4Cl, NH_4OH, NH_4HS, warm well, and filter.</td></tr>
<tr><td colspan="4">Ppt. Hg, Bi, Cu, Cd.
Wash, boil with HNO_3 (sp. gr. 1.20), filter.</td><td colspan="2" rowspan="2">Filt. As, Sb, Sn, Au, Pt.
Acidify with HCl, agitate, filter (disregard the filtrate), boil the ppt. with strong HCl, filter.</td><td colspan="7">Ppt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni.
Wash, dissolve in 2 parts HCl and 1 part HNO_3, evaporate almost to dryness, add H_2O and then NH_4OH in excess, and filter.</td><td colspan="6">Filt. Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Evaporate to remove NH_4HS, add $(NH_4)_2CO_3$, boil, filter.</td></tr>
<tr><td rowspan="4">Ppt. Hg.
Black. Confirm by Cu test.</td><td colspan="3">Filt. Bi, Cu, Cd.
Add NH_4OH in excess, and filter.</td><td colspan="3">Ppt. Fe, Ce, Al, Cr.
Wash, allow to drain, fuse on foil with Na_2CO_3 and KNO_3, boil cooled mass with H_2O, decant upon a filter.</td><td colspan="4">Filt. Mn, Zn, Co, Ni.
Acidify slightly with $HC_2H_3O_2$, add H_2S, filter.</td><td colspan="3">Ppt. Ba, Sr, Ca.
Wash, dissolve in $HC_2H_3O_2$, dilute, add K_2CrO_4, filter.</td><td colspan="3">Filt. Mg, K, Na, Li, NH_4.
Add $(NH_4)_2HPO_4$, agitate, filter.</td></tr>
<tr><td rowspan="3">Ppt. Bi.
White. Confirm by BiOCl test.</td><td colspan="2">Filt. Cu, Cd.
Blue, if Cu be present. Add H_2S. If ppt. be dark, filter (disregard filtrate), wash ppt., boil with 1 part H_2SO_4 and 10 parts H_2O, and filter.</td><td rowspan="3">Ppt. As, Au, Pt.
Separate by chart, p. 35.</td><td rowspan="3">Filt. Sb, Sn.
Separate by chart, p. 35.</td><td rowspan="3">Ppt. Fe, Ce.
Separate according to chart, p. 27.</td><td colspan="2">Filt. Al, Cr.
Yellow, if Cr be present. Divide into two portions.</td><td colspan="3">Ppt. Zn, Co, Ni.
Wash, dissolve in 2 parts HCl and 1 part HNO_3, evaporate almost to dryness, add H_2O and then KOH until distinctly alkaline, filter.</td><td rowspan="3">Filt. Mn.
Add NH_4OH in excess and H_2S. Flesh-colored ppt. Apply Crum's test to original solution.</td><td rowspan="3">Ppt. Ba.
Yellow.</td><td colspan="2">Filt. Sr, Ca.
Add very dilute H_2SO_4, allow to stand, filter.</td><td rowspan="3">Ppt. Mg.
White, crystalline.</td><td colspan="2">Filt. K, Na, Li, NH_4.
Add Na_2HPO_4 and NaOH, boil until all NH_3 is expelled, and filter.</td></tr>
<tr><td rowspan="2">Ppt. Cu.
Black.</td><td rowspan="2">Filt. Cd.
Dilute and add H_2S. Yellow ppt.</td><td rowspan="2">Al.
Add NH_4Cl, warm well, and allow to stand. White, gelatinous ppt.</td><td rowspan="2">Cr.
Acidify with $HC_2H_3O_2$ and add $Pb(A)_2$. Yellow ppt.</td><td colspan="2">Ppt. Co, Ni.
Wash, dissolve in HCl, evaporate almost to dryness, add H_2O, and treat with KCN and HCl according to chart, p. 22, then add KOH until alkaline, filter.</td><td rowspan="2">Filt. Zn.
Add NH_4HS, warm, allow to stand. White ppt.</td><td rowspan="2">Ppt. Sr.
White. Confirm by flame test.</td><td rowspan="2">Filt. Ca.
Add NH_4OH in excess and $(NH_4)_2C_2O_4$. White ppt.</td><td rowspan="2">Ppt. Li.
White. Confirm by flame test.</td><td rowspan="2">Filt. K, Na.
Acidify with $HC_2H_3O_2$, add $Co_2(NO_2)_6 \cdot 6NaNO_2$. Yellow ppt. indicates K.†</td></tr>
<tr><td>Ppt. Ni.
Green. Confirm by borax bead.</td><td>Filt. Co.
Evaporate to dryness and test with borax bead.</td></tr>
</table>

* See notes on following page.

† Test original solution for Na and NH_4.

NOTES ON THE PRECEDING CHART.

1. To digest the sulphides of Groups V. and VI. with $(NH_4)_2S$, it is best to wash the precipitate into a dish by means of a jet of water from the wash-bottle, and, after decanting the excess of water and adding the $(NH_4)_2S$, to warm but slightly.

When Sn, Au, and Pt are to be detected, the yellow ammonium sulphide, $(NH_4)_2S$, must be used to insure solution of the sulphides of these bases; but when As and Sb are the only metals of this group to be sought, NH_4HS may be used with equally good results.

2. When Cu is present, some of its sulphide may be dissolved in the process of digesting, so that any dark precipitate obtained upon acidifying the $(NH_4)_2S$ or NH_4HS with HCl should be tested for Cu.

Group VII. Silver, Mercury(ous), Lead.

REACTIONS OF SOLUBLE SALTS OF SILVER.

Use a 1-per-cent. solution of silver nitrate, $AgNO_3$.

1. HCl or a soluble chloride precipitates white, curdy **silver chloride, AgCl.**

$$AgNO_3 + HCl = AgCl + HNO_3.$$

This precipitate is insoluble in HNO_3, but soluble in NH_4OH, forming **ammonio-silver chloride,** $(AgCl)_2(NH_3)_3$.

$$2AgCl + 3NH_4OH = (AgCl)_2(NH_3)_3 + 3H_2O.$$

From this solution AgCl is again precipitated by acidifying with HNO_3.

$$(AgCl)_2(NH_3)_3 + 3HNO_3 = 2AgCl + 3NH_4NO_3.$$

2. H_2S or NH_4HS produces a black precipitate of **silver sulphide,** Ag_2S, soluble in boiling HNO_3.

3. KOH or NaOH forms a grayish-brown precipitate of **silver oxide,** Ag_2O, insoluble in excess of the reagent.

$$2AgNO_3 + 2KOH = Ag_2O + 2KNO_3 + H_2O.$$

4. NH_4OH in small quantity precipitates Ag_2O, soluble in excess of the reagent.

5. K_2CrO_4 produces a red precipitate of **silver chromate,** Ag_2CrO_4, soluble in HNO_3 or NH_4OH.

6. KI and KBr cause respectively precipitates of yellow **silver iodide,** AgI, insoluble in HNO_3 or NH_4OH, and yellowish-

white **silver bromide,** AgBr, insoluble in HNO_3, but slowly soluble in NH_4OH.

7. KCN precipitates white **silver cyanide,** AgCN, soluble in excess of the reagent.

8. Heated with Na_2CO_3 on charcoal, before the blowpipe, compounds of silver yield a bright metallic button of **silver, Ag,** soluble in HNO_3.

REACTIONS OF SOLUBLE MERCUROUS SALTS.

Use a 1-per-cent. solution of mercurous nitrate, $Hg_2(NO_3)_2 \cdot 2H_2O$.

1. HCl or a soluble chloride precipitates white **mercurous chloride,** Hg_2Cl_2, converted by strong HNO_3 into a mixture of **mercuric chloride,** $HgCl_2$, and **mercuric nitrate,** $Hg(NO_3)_2$. It also becomes black on the addition of NH_4OH, owing to formation of **mercurous ammonium chloride,** NH_2Hg_2Cl.

$$Hg_2Cl_2 + 2NH_4OH = NH_2Hg_2Cl + 2H_2O + NH_4Cl.$$

2. H_2S or NH_4HS precipitates a black mixture of **mercury,** Hg, and **mercuric sulphide,** HgS.

$$Hg_2(NO_3)_2 + H_2S = Hg + HgS + 2HNO_3.$$

3. KOH or NaOH produces a black precipitate of **mercurous oxide,** Hg_2O, insoluble in excess of the reagent.

4. NH_4OH causes a black precipitate of **mercurous ammonium nitrate,** $NH_2Hg_2NO_3$, insoluble in excess of the reagent.

5. K_2CrO_4 forms an orange-colored precipitate of **mercurous chromate,** Hg_2CrO_4.

6. KI precipitates green **mercurous iodide,** Hg_2I_2.

7. Before the blowpipe mercurous salts volatilize, some being converted into a mercuric salt and mercury, both of which sublime.

REACTIONS OF SOLUBLE SALTS OF LEAD.

Use a 1-per-cent. solution of lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$.

1. HCl or a soluble chloride produces a white, crystalline precipitate of **lead chloride,** $PbCl_2$, which is quite freely soluble in hot water, and sparingly in cold.

2. H_2S or NH_4HS precipitates black **lead sulphide,** PbS, insoluble in $(NH_4)_2S$ or NH_4HS, but soluble in hot HNO_3.

3. KOH or NaOH produces a white precipitate of **lead hydrate,** $Pb(OH)_2$, soluble in large excess of reagent to form **potassium** or **sodium plumbate,** $Pb(OK)_2$ or $Pb(ONa)_2$.

4. NH_4OH precipitates white **basic lead hydrate,** insoluble in excess of the reagent.

5. K_2CrO_4 produces a yellow precipitate of **lead chromate,** $PbCrO_4$, known as **chrome-yellow.** It is soluble in KOH or HNO_3.

6. KI forms a yellow precipitate of **lead iodide,** PbI_2, soluble in boiling water.

7. H_2SO_4 produces a white precipitate of **lead sulphate,** $PbSO_4$, insoluble in acids, except when concentrated and hot, but soluble in $NH_4C_2H_3O_2$ or $(NH_4)_2C_4H_4O_6$.

8. Na_2CO_3 precipitates white **basic lead carbonate,** $(PbCO_3)_2Pb(OH)_2$.

9. Before the blowpipe, on charcoal, lead compounds yield a malleable globule of **lead,** Pb, with the formation of an incrustation of yellow **lead oxide,** PbO.

CHART FOR THE DETECTION OF THE BASES IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP VII.

<table>
<tr><td colspan="3">Completely precipitate the original solution with dilute HCl, filter (disregard the filtrate), wash the ppt. with a small quantity of cold H_2O (disregard the washings also), then pour on the filter boiling H_2O.</td></tr>
<tr><td colspan="2">Precipitate Ag, Hg(ous).
Pour on the filter NH_4OH.</td><td rowspan="2">Filtrate Pb.
Add dilute H_2SO_4 and allow to cool. White ppt.</td></tr>
<tr><td>Ppt. Hg(ous).
Black.</td><td>Filt. Ag.
Acidify with HNO_3.
White, curdy ppt.*</td></tr>
</table>

NOTES ON THE FOLLOWING CHART.

1. Before commencing the analysis of a solution, its action on litmus paper must always be noted. If alkaline a precipitate may be caused by HCl, on account of the presence of substances held in solution by alkalies, as, for instance, As_2S_3 in $(NH_4)_2CO_3$, or AgCl in NH_4OH. Silicic acid from alkali silicates may likewise be precipitated; when the latter are present it is neces-

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* The presence of Hg_2Cl_2 may interfere with the solvent action of NH_4OH on AgCl. If, then, Hg(ous) is present and no precipitate for Ag is obtained, wash the NH_2Hg_2Cl, transfer it to a dish, boil with HNO_3 till almost dry, add H_2O, and then dilute HCl to test for Ag.

sary to precede the addition of HCl by evaporation to dryness with HNO_3, adding water, filtering out the insoluble silica, and proceeding with the filtrate in the manner described below, commencing with the addition of HCl.

2. Besides causing the precipitation of such substances as mentioned above, HCl more frequently throws down basic salts of Bi and Sb ; these are, however, readily distinguished from the bases of Group VII. by dissolving on the further addition of HCl. Aside from this contingency, the original solution may be turbid from the presence of a precipitate of the bases of Group VII., of the basic salts cited, or of some compound decomposable by HCl.

It will therefore be found best before undertaking the precipitation of the bases of Group VII. to make a preliminary test for their presence by adding to a small quantity of the original solution an equal volume of dilute HCl. If no precipitate is produced by this reagent, or if at first formed it is redissolved, or if originally present it is dissolved, the absence of the bases of Group VII. is indicated ; in which case, after the addition of a few drops of HCl to a larger portion of the original solution, the detection of the bases of the first six groups can be at once proceeded with according to the following chart.

But, on the contrary, if a permanent precipitate is produced by the equal volume of dilute HCl, or, if originally present, remains undissolved, one or more bases of Group VII. are shown to be present ; in which instance the analysis is begun by removing these from a larger portion of the original solution according to the following chart.

3. On account of the slight solubility of $PbCl_2$ in water, Pb may be found both in Groups VII. and VI. ; to reduce the amount held in solution to a minimum the precipitation by HCl should be performed in the cold.

4. When the presence of HNO_3 is suspected, the filtrate, after the precipitation of Group VII. and before the addition of H_2S, should be evaporated to dryness to expel the HNO_3. After the residue has been dissolved in the original bulk of water and acidified with a few drops of HCl, the H_2S may be added and the analysis continued according to the following chart.

5. Care must be exercised in separating Pb as $PbSO_4$ in Group VI., as Bi is likely to be thrown down as $(BiO)NO_3$ upon evaporation of the HNO_3 and addition of H_2O. $(BiO)NO_3$ may be distinguished from $PbSO_4$ by dissolving readily in dilute HNO_3.

CHART FOR THE DETECTION OF BASES IN SOLUTIONS CONTAINING SOLUBLE SALTS OF ALL FOREGOING ELEMENTS.

<table>
<tr><td colspan="23">Ag, Hg(ous), Pb, Hg(ic), Bi, Cu, Cd, As, Sb, Sn, Au, Pt, Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
To a small portion of the original solution add an equal volume of dilute HCl. If a ppt. remains undissolved, take a larger portion and add sufficient dilute HCl to completely precipitate it, filter.</td></tr>
<tr><td colspan="3">Ppt. Ag, Hg(ous), Pb.
Wash with a very small quantity of cold H_2O, and pour on the filter boiling H_2O.</td><td colspan="20">Filt. Hg(ic), Pb, Bi, Cu, Cd, As, Sb, Sn, Au, Pt, Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Evaporate almost to dryness, add H_2O, acidify with HCl, and then add H_2S until, after warming, the mixture smells strongly of it, filter.</td></tr>
<tr><td colspan="2">Ppt. Ag, Hg(ous).
Pour on the filter NH_4OH.</td><td rowspan="6">Filt. Pb.
Add dilute H_2SO_4, allow to cool. White ppt.</td><td colspan="7">Ppt. Hg, Pb, Bi, Cu, Cd, As, Sb, Sn, Au, Pt.
Wash, digest with $(NH_4)_2S$, filter.</td><td colspan="13">Filt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni, Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Add NH_4Cl, NH_4OH, NH_4HS, warm well, and filter.</td></tr>
<tr><td rowspan="5">Ppt. Hg(ous)
Black.</td><td rowspan="5">Filt. Ag.
Acidify with HNO_3. White, curdy ppt. See footnote on page 45.</td><td colspan="5">Ppt. Hg, Pb, Bi, Cu, Cd.
Wash, boil with HNO_3, filter.</td><td colspan="2">Filt. As, Sb, Sn, Au, Pt.
Acidify with dilute HCl, shake well, filter, disregard filtrate, wash ppt., boil it with strong HCl, filter.</td><td colspan="7">Ppt. Fe, Ce, Al, Cr, Mn, Zn, Co, Ni.
Wash, dissolve in 2 parts HCl and 1 part HNO_3, evaporate almost to dryness, add H_2O, and then NH_4OH in excess, agitate, and filter.</td><td colspan="6">Filt. Ba, Sr, Ca, Mg, K, Na, Li, NH_4.
Evaporate to remove NH_4HS, add $(NH_4)_2CO_3$, boil, filter.</td></tr>
<tr><td rowspan="4">Ppt. Hg.
Black. Confirm by Cu test.</td><td colspan="4">Filt. Pb, Bi, Cu, Cd.
Add two drops of dilute H_2SO_4, evaporate to a small bulk, dilute with H_2O, filter.</td><td rowspan="4">Ppt. As, Au, Pt.
Separate by chart, page 35</td><td rowspan="4">Filt. Sb, Sn.
Separate by chart, page 35.</td><td colspan="3">Ppt. Fe, Ce, Al, Cr.
Wash, allow to drain; fuse on foil with Na_2CO_3 and KNO_3, boil cooled mass with H_2O, decant upon a filter.</td><td colspan="4">Filt. Mn, Zn, Co, Ni.
Acidify slightly with $HC_2H_3O_2$, add H_2S, and filter.</td><td colspan="3">Ppt. Ba, Sr, Ca.
Wash, dissolve in $HC_2H_3O_2$, dilute, add K_2CrO_4, and filter.</td><td colspan="3">Filt. Mg, K, Na, Li, NH_4.
Add $(NH_4)_2HPO_4$, agitate, and filter.</td></tr>
<tr><td rowspan="3">Ppt. Pb.
White.</td><td colspan="3">Filt. Bi, Cu, Cd.
Add NH_4OH in excess, filter.</td><td rowspan="3">Ppt. Fe, Ce.
Separate according to chart, page 27.</td><td colspan="2">Filt. Al, Cr.
Yellow, if Cr be present. Divide into two portions.</td><td colspan="3">Ppt. Zn, Co, Ni.
Wash, dissolve in HCl and HNO_3, evaporate almost to dryness, add H_2O, and then KOH until alkaline, filter.</td><td rowspan="3">Filt. Mn.
Add NH_4OH until alkaline and H_2S. Flesh-colored ppt. Apply Crum's test to original solution.</td><td rowspan="3">Ppt. Ba.
Yellow.</td><td colspan="2">Filt. Sr, Ca.
Add very dilute H_2SO_4, allow to stand, filter.</td><td rowspan="3">Ppt. Mg.
White, crystalline.</td><td colspan="2">Filt. K, Na, Li, NH_4.
Add Na_2HPO_4 and NaOH, boil until all NH_3 is expelled, and filter.</td></tr>
<tr><td rowspan="2">Ppt. Bi.
White. Confirm by BiOCl test.</td><td colspan="2">Filt. Cu, Cd.
Blue, if Cu be present. Add H_2S; if ppt. be dark, filter, disregard filtrate, wash ppt., boil it with dilute H_2SO_4, filter.</td><td rowspan="2">Al.
Add NH_4Cl, warm well, and allow to stand. White, gelatinous ppt.</td><td rowspan="2">Cr.
Acidify with $HC_2H_3O_2$, and add $Pb(\bar{A})_2$. Yellow ppt.</td><td colspan="2">Ppt. Co, Ni.
Wash, dissolve in HCl, evaporate almost to dryness, add H_2O, treat with KCN and HCl, according to chart, page 22, add KOH until alkaline, filter.</td><td rowspan="2">Filt. Zn.
Add NH_4HS, warm, allow to stand. White ppt.</td><td rowspan="2">Ppt. Sr.
White. Confirm by flame test.</td><td rowspan="2">Filt. Ca.
Add NH_4OH in excess and $(NH_4)_2C_2O_4$. White ppt.</td><td rowspan="2">Ppt. Li.
Confirm by flame test.</td><td>Filt. K, Na.
Acidify with $HC_2H_3O_2$, add $Co_2(NO_2)_6 \cdot 6NaNO_2$. Yellow ppt. indicates K.</td></tr>
<tr><td>Ppt. Cu.
Black.</td><td>Filt. Cd.
Dilute, add H_2S. Yellow ppt.</td><td>Ppt. Ni.
Green. Confirm by borax bead.</td><td>Filt. Co.
Evaporate to dryness and test with borax bead.</td><td>Test original solution for Na and NH_4.</td></tr>
</table>

CHAPTER III.

THE REACTIONS AND DETECTION OF ACIDS.

Group I. Hydrochloric Acid, Hydrobromic Acid, Hydriodic Acid, Hydrofluoric Acid, Hydrocyanic Acid.

REACTIONS OF SOLUBLE SALTS OF HYDROCHLORIC ACID.

Use a 1-per-cent. solution of potassium chloride, KCl.

1. $AgNO_3$ produces a white, curdy precipitate of **silver chloride,** AgCl, insoluble in HNO_3, but readily soluble in NH_4OH. See reaction No. 1 under silver.

This precipitate should be preserved to compare with the corresponding ones obtained in the reactions of hydrobromic, hydriodic, and hydrocyanic acids.

2. $Hg_2(NO_3)_2$ causes a white precipitate of **mercurous chloride,** Hg_2Cl_2, insoluble in HNO_3, and blackened by the addition of NH_4OH.

3. $Pb(C_2H_3O_2)_2$ forms a white, crystalline precipitate of **lead chloride,** $PbCl_2$, soluble in excess of water.

4. H_2SO_4, warmed with the solution, liberates **hydrochloric acid,** HCl.

$$2KCl + H_2SO_4 = 2HCl + K_2SO_4.$$

This compound may be recognized by its odor and the strongly acid reaction of its vapor, also by the dense, white fumes of NH_4Cl produced by holding a glass rod moistened with NH_4OH near the mouth of the test-tube.

5. H_2SO_4 and MnO_2, added to the solution and the mixture warmed, cause the evolution of **chlorine,** Cl, identified by its odor and color.

$$2KCl + 2H_2SO_4 + MnO_2 = Cl_2 + K_2SO_4 + MnSO_4 + 2H_2O.$$

REACTIONS OF SOLUBLE SALTS OF HYDROBROMIC ACID.

Use a 1-per-cent. solution of potassium bromide, KBr.

1. $AgNO_3$ produces a yellowish-white precipitate of **silver bromide,** AgBr, insoluble in HNO_3, and but very sparingly soluble in NH_4OH.

2. $Hg_2(NO_3)_2$ precipitates yellowish-white **mercurous bromide,** Hg_2Br_2.

3. H_2SO_4 and MnO_2, warmed with the solution, cause the evolution of red vapors of **bromine**, Br, the odor of which is very irritating.

4. Chlorine water liberates Br

$$2KBr + Cl_2 = Br_2 + 2KCl.$$

If starch paste be added to the mixture, a yellow color due to the formation of **starch bromide** results. When this test is applied to very dilute solutions, it is necessary to agitate the mixture with ether or chloroform, which will dissolve the Br, and upon separating from the water will exhibit a yellowish-red color if that element be present.

REACTIONS OF SOLUBLE SALTS OF HYDRIODIC ACID.

Use a 1-per-cent. solution of potassium iodide, KI.

1. $AgNO_3$ produces a yellowish precipitate of **silver iodide**, AgI, insoluble in HNO_3 or NH_4OH.

2. $Hg_2(NO_3)_2$ precipitates green **mercurous iodide**, Hg_2I_2.

3. $HgCl_2$ causes a red precipitate of **mercuric iodide**, HgI_2, soluble in an excess of either substance.

4. $Pb(C_2H_3O_2)_2$ produces a yellow precipitate of **lead iodide**, PbI_2, soluble in boiling water.

5. Chlorine water liberates **iodine**, I, which produces with starch paste a blue color of **starch iodide**. The color disappears on heating, but reappears on cooling; it is permanently discharged by an excess of chlorine water, through the formation of colorless **iodine chloride**.

6. $CuSO_4$, in concentrated solution, produces in a solution of KI a white precipitate of **cuprous iodide**, Cu_2I_2, which is colored dark by the iodine set free in the reaction.

$$4KI + 2CuSO_4 = Cu_2I_2 + I_2 + 2K_2SO_4.$$

When, however, a reducing agent, such, for instance, as $FeSO_4$, is added at the same time, the liberation of I is prevented and the true color of the Cu_2I_2 is obtained.

$$2KI + 2CuSO_4 + 2FeSO_4 = Cu_2I_2 + K_2SO_4 + Fe_2(SO_4)_3.$$

HYDROFLUORIC ACID, HF.

The evolution of intensely irritating fumes, on the addition of H_2SO_4 to calcium fluoride, which etch glass, is sufficiently characteristic of this acid. AgF is soluble in H_2O.

REACTIONS OF SOLUBLE SALTS OF HYDROCYANIC ACID.

Use a 1-per-cent. solution of potassium cyanide, KCN.

1. $AgNO_3$ produces a white precipitate of **silver cyanide,** AgCN, soluble in KCN, sparingly soluble in NH_4OH, and insoluble in dilute HNO_3.

2. NH_4HS evaporated with KCN to dryness, at a temperature below boiling, will give, on dissolving the residue in water and adding Fe_2Cl_6, a deep blood-red color of $Fe_2(CNS)_6$, produced from the sulphocyanate formed during the evaporation.

3. $FeSO_4$ and Fe_2Cl_6, when added to the solution and followed with NaOH until a permanent precipitate is produced, will, after heating the mixture and acidifying it with HCl, produce a deep blue precipitate of **ferric ferrocyanide,** $(Fe_2)_2(Fe(CN)_6)_3$.

$$6KCN + FeSO_4 = K_4Fe(CN)_6 + K_2SO_4.$$

$$Fe_2Cl_6 + FeSO_4 + 8NaOH = Fe_2(OH)_6 + Fe(OH)_2 + 6NaCl + Na_2SO_4.$$

$$2Fe_2(OH)_6 + 3K_4Fe(CN)_6 + 12HCl = (Fe_2)_2(Fe(CN)_6)_3 + 12KCl + 12H_2O.$$

4. HCl, HNO_3, or any other acid, causes an evolution of **hydrocyanic acid,** HCN, readily recognized by its odor. Great care should be exercised in carrying out this test in order to avoid inhaling more than a trace of the fumes.

DIRECTIONS FOR THE DETECTION OF THE ACIDS IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP I.

To some of the original solution add a small crystal of $FeSO_4$, some solution of Fe_2Cl_6, and then sufficient NaOH to make the mixture alkaline. Heat and afterwards acidify with HCl; a deep blue precipitate indicates HCN.

If HCN is present, add to another portion of the original solution HNO_3 and boil until all HCN is expelled.

To the solution thus treated, or, when HCN is absent, to some of the original solution simply acidified with HNO_3, add $AgNO_3$; warm the mixture, shake well, and continue the addition of $AgNO_3$ until the precipitation is completed. Collect the precipitate of AgCl, AgBr, and AgI on a filter, wash, and pour upon the filter NH_4OH; AgCl will be dissolved, and may be detected in the filtrate by acidifying with HNO_3. Its presence indicates HCl.

To a third portion of the original solution add a few drops of starch paste, and then, slowly, chlorine water until, after agitation, the liquid smells of it. If a blue color is obtained HI is present. Continue the addition of chlorine water until the blue color is destroyed, when, if the solution is yellow, HBr is indicated. Its presence may be still further verified by agitating the solution with chloroform, which will dissolve the bromine, and upon separating exhibit a yellowish-red color.

NOTE.—Although slight acidity with HCl is not objectionable, alkaline and strongly acid solutions should always be rendered neutral before applying the starch and chlorine test.

Group II. Hypochlorous Acid, Chloric Acid, Hydrosulphuric Acid, Sulphurous Acid, Sulphuric Acid, Thiosulphuric Acid, Nitric Acid, Hypophosphorous Acid, Orthophosphoric Acid, Pyrophosphoric Acid, Metaphosphoric Acid, Boric Acid, Carbonic Acid, Silicic Acid.

REACTIONS OF SOLUBLE SALTS OF HYPOCHLOROUS ACID.

Use a 2-per-cent. solution of sodium hypochlorite, $NaClO$.

1. HCl causes the evolution of **chlorine,** Cl, readily recognized by its odor and by the bleaching action it exerts on litmus paper or on solution of indigo.

$$NaClO + 2HCl = Cl_2 + NaCl + H_2O.$$

2. $AgNO_3$ produces a white precipitate of **silver chloride,** $AgCl$, insoluble in HNO_3, but soluble in NH_4OH.

$$3NaClO + 3AgNO_3 = 2AgCl + AgClO_3 + 3NaNO_3.$$

3. $Pb(C_2H_3O_2)_2$, with an excess of the solution, forms at first a white precipitate which, on heating, turns brown, owing to the formation of **lead peroxide,** PbO_2.

$$9NaClO + Pb(C_2H_3O_2)_2 = PbO_2 + 9NaCl + 4CO_2 + 3H_2O.$$

REACTIONS OF SOLUBLE SALTS OF CHLORIC ACID.

Use a 5-per-cent. solution of potassium chlorate, $KClO_3$.

1. H_2SO_4 causes the evolution of yellow **chlorine tetroxide,** having a characteristic odor.

$$3KClO_3 + 2H_2SO_4 = Cl_2O_4 + KClO_4 + 2KHSO_4 + H_2O.$$

When the dry salt is used this reaction takes place with some violence, or, when organic matter is present, with explosion.

2. On heating the dry salt **oxygen,** O, is given off, and may

be readily detected by holding over the mass the glowing end of a match or taper, which is rekindled by the oxygen.

3. $AgNO_3$ produces no precipitate. This is an important distinction from HCl. When it is present it may be removed by just enough $AgNO_3$ to precipitate it, and the remaining solution after filtration tested for $HClO_3$ by evaporating to dryness, heating to redness, dissolving in water, and adding $AgNO_3$, when, if a chlorate was present, a white precipitate of **silver chloride,** AgCl, will form; the chlorate having been converted by heat into chloride.

$$KClO_3 = KCl + O_3.$$

4. A modification of the above test may be used to distinguish a chlorate from a nitrate, as the latter gives many of the reactions of the former. The residue, after heating a nitrate, will not give a precipitate when dissolved in water and tested with $AgNO_3$.

5. $AgNO_3$, with a drop or two of strong H_2SO_4, will cause a precipitate of AgCl, owing to the decomposition of the chlorate by the strong acid.

HYDROSULPHURIC ACID, H_2S.

Hydrogen Sulphide.

When occurring in moderate amount, sufficient evidence of the presence of this acid is afforded by its characteristic odor. This is at once noticeable in the original material when the acid exists uncombined, but, in the case of sulphides, only after the application of H_2SO_4, and sometimes of heat also.

A trace may be detected by holding over the mouth of the test-tube a piece of filter paper moistened with a drop of solution of lead acetate, when, if H_2S be present, the moistened spot will become black from the formation of lead sulphide.

REACTIONS OF SOLUBLE SALTS OF SULPHUROUS ACID.

Use a 2-per-cent. solution of sodium sulphite, $Na_2SO_3.7H_2O$.

1. In the free state, sulphurous acid, H_2SO_3, may be considered a solution of sulphur dioxide, SO_2, in water, and is recognized by the odor of burning sulphur, which is characteristic of SO_2. The uncombined acid has also strong bleaching action, and readily decolorizes potassium permanganate solution.

$$5H_2SO_3 + K_2Mn_2O_8 = K_2SO_4 + 2MnSO_4 + 2H_2SO_4 + 3H_2O.$$

2. Sulphites are characterized by yielding SO_2 on the addition of a strong acid.

$$Na_2SO_3 + H_2SO_4 = SO_2 + Na_2SO_4 + H_2O.$$

If a piece of filter paper moistened with a drop of lead acetate solution be held over the mouth of the test-tube, no change will occur; but, if this be replaced by one moistened with a drop of mercurous nitrate solution, a blackish color due to metallic **mercury**, Hg, results.

$$4SO_2 + Hg_2(NO_3)_2 + 4H_2O = Hg_2 + 4H_2SO_4 + N_2O_2.$$

3. When the free acid or a sulphite is added to a mixture of zinc and hydrochloric acid, **hydrogen sulphide**, H_2S, is evolved.

$$SO_2 + 3H_2 = H_2S + 2H_2O.$$

4. $BaCl_2$ in neutral solution causes a white precipitate of **barium sulphite**, $BaSO_3$, soluble in HCl.

5. $ZnSO_4$ and $Na_2Fe(NO)(CN)_5$ produce, in dilute solutions of sulphites, a red color, or, in more concentrated solutions, a flocculent reddish precipitate. A few drops of potassium ferrocyanide solution render the reaction more distinct.

REACTIONS OF SOLUBLE SALTS OF SULPHURIC ACID.

Use a 1-per-cent. solution of sodium sulphate, $Na_2SO_4 . 10H_2O$.

1. $BaCl_2$ produces a white precipitate of **barium sulphate**, $BaSO_4$, insoluble in boiling HCl or HNO_3.

2. $Pb(C_2H_3O_2)_2$ causes a precipitate of white **lead sulphate**, $PbSO_4$, insoluble in dilute acids, but soluble in hot concentrated acids.

3. When a sulphate is fused on charcoal with Na_2CO_3 and the fused mass placed on a bright silver coin and moistened with a drop of dilute HCl, a black stain, due to the formation of **silver sulphide**, Ag_2S, results. This reaction is especially adapted to the detection of insoluble sulphates.

REACTIONS OF SOLUBLE SALTS OF THIOSULPHURIC ACID.

Use a 2-per-cent. solution of sodium thiosulphate, $Na_2S_2O_3 . 5H_2O$.

1. H_2SO_4 causes the evolution of **sulphur dioxide**, SO_2, and a precipitation of **sulphur**, S; the latter feature distinguishes this acid from sulphurous acid.

$$Na_2S_2O_3 + H_2SO_4 = SO_2 + S + Na_2SO_4 + H_2O.$$

2. $AgNO_3$ produces a white precipitate of **silver thiosulphate,** $Ag_2S_2O_3$, soluble in excess. After a time (immediately on heating) the precipitate becomes dark and then black, **silver sulphide,** Ag_2S, and sulphuric acid being formed.

$$Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4.$$

3. $BaCl_2$ produces a white precipitate of **barium thiosulphate,** BaS_2O_3, soluble in excess of water, and decomposed by HCl with the precipitation of sulphur.

4. Added to a mixture of zinc and hydrochloric acid, **hydrogen sulphide,** H_2S, is evolved.

REACTIONS OF SOLUBLE SALTS OF NITRIC ACID.

Use a 2-per-cent. solution of potassium nitrate, KNO_3.

1. H_2SO_4, on heating, liberates **nitric acid,** HNO_3. If copper turnings be added with the sulphuric acid, colorless **nitrogen dioxide,** N_2O_2, will be given off, which in contact with air absorbs oxygen to form red **nitrogen tetroxide,** N_2O_4, which is readily recognized by its color and odor.

$$8HNO_3 + 3Cu = N_2O_2 + 3Cu(NO_3)_2 + 4H_2O;$$
$$N_2O_2 + O_2 = N_2O_4.$$

If alcohol be added to the mixture, the characteristic odor of nitrous ether is developed.

2. $FeSO_4$, acidified with H_2SO_4, added in a test-tube, so as to form a layer on a solution of a nitrate acidified with H_2SO_4, will cause a dark layer to form at the line of contact.

3. $(C_6H_5)_2NH$ applied in like manner gives a deep-blue color.

4. Indigo solution is decolorized by free nitric acid, or by a solution of a nitrate strongly acidified with H_2SO_4.

5. When a nitrate is added to a mixture of zinc and potassium hydrate, the nitric acid is reduced to **ammonia,** NH_3, which is vaporized, and may be detected in the usual way.

$$HNO_3 + 4H_2 = NH_3 + 3H_2O.$$

This is a valuable test for distinguishing nitric acid in the presence of chloric acid.

6. Heated on charcoal, deflagration takes place, the charcoal burning at the expense of the oxygen of the nitrate.

7. On adding KI and starch paste to a solution of a nitrate and acidifying the mixture with $HC_2H_3O_2$, no blue color of **starch iodide** is produced (a distinction from nitrites).

REACTIONS OF SOLUBLE SALTS OF HYPOPHOSPHOROUS ACID.

Use a 2-per-cent. solution of sodium hypophosphite, $NaPH_2O_2 \cdot H_2O$.

1. By ignition the hypophosphites are resolved into spontaneously inflammable **hydrogen phosphide**, H_3P, and phosphates.

$$2NaPH_2O_2 = H_3P + Na_2HPO_4.$$

2. $AgNO_3$ produces at first a white precipitate of **silver hypophosphite**, $AgPH_2O_2$, which soon becomes black, owing to the formation of metallic **silver**, Ag.

$$2NaPH_2O_2 + 2AgNO_3 = Ag_2 + 2NaH_2PO_4 + N_2O_3.$$

3. $HgCl_2$ in excess causes a white precipitate of **mercurous chloride**, Hg_2Cl_2. This reaction takes place more rapidly on warming and in the presence of HCl.

$$NaPH_2O_2 + 4HgCl_2 + 2H_2O = 2Hg_2Cl_2 + NaH_2PO_4 + 4HCl.$$

4. $CuSO_4$, upon boiling, produces in solutions of hypophosphites acidified with H_2SO_4 a brownish precipitate of **copper**, Cu (a distinction from phosphorous acid).

REACTIONS OF SOLUBLE SALTS OF ORTHOPHOSPHORIC ACID.

Use a 2-per-cent. solution of sodium phosphate, $Na_2HPO_4 \cdot 12H_2O$.

1. $AgNO_3$ causes a light-yellow precipitate of **silver phosphate**, Ag_3PO_4, soluble in HNO_3 or NH_4OH.

2. Fe_2Cl_6, in the presence of sodium acetate, produces a yellowish-white, gelatinous precipitate of **ferric phosphate**, $Fe_2(PO_4)_2$. An excess of Fe_2Cl_6 must be avoided.

3. $(NH_4)_2MoO_4$, in neutral or acid solution, causes a yellow precipitate of **ammonium phosphomolybdate**, $(NH_4)_3PO_4(MoO_3)_{12}$, to separate slowly. This compound is insoluble in HNO_3, but dissolves in NH_4OH. The precipitation is promoted by the presence of NH_4NO_3, which serves to counteract the tendency of other compounds to retard the formation.

4. Magnesia mixture (consisting of $MgSO_4$, NH_4Cl, and NH_4OH) causes a white precipitate of **magnesium ammonium phosphate**, $Mg(NH_4)PO_4$. Agitation facilitates the formation of this precipitate.

5. $BaCl_2$, in neutral solution, produces a white precipitate of **barium phosphate**, $BaHPO_4$, soluble in HCl.

6. Albumen (white of egg) does not cause a precipitate.

REACTIONS OF SOLUBLE SALTS OF PYROPHOSPHORIC ACID.

Use a 2-per-cent. solution of sodium pyrophosphate, $Na_4P_2O_7.10H_2O$.

1. $AgNO_3$ precipitates white **silver pyrophosphate**, $Ag_4P_2O_7$, soluble in HNO_3 or NH_4OH.

2. $MgSO_4$ causes a white precipitate of **magnesium pyrophosphate**, $Mg_2P_2O_7$, soluble in excess of the reagent. From this solution a mixture of NH_4OH and NH_4Cl does not reprecipitate it in the cold. This behavior may be used to distinguish ortho- from pyrophosphoric acid.

3. $(NH_4)_2MoO_4$ produces no precipitate.

4. Albumen does not cause a precipitate.

5. $BaCl_2$, in neutral solution, precipitates white **barium pyrophosphate**, $Ba_2P_2O_7$, soluble in HCl.

6. Pyrophosphoric acid is converted into orthophosphoric by boiling its solution. This conversion takes place more readily in the presence of HNO_3.

REACTIONS OF SOLUBLE SALTS OF METAPHOSPHORIC ACID.

Use a 2-per-cent. solution of sodium metaphosphate, $NaPO_3$.

1. $AgNO_3$ produces a white precipitate of **silver metaphosphate**, $AgPO_3$, soluble in HNO_3 or NH_4OH.

2. Albumen forms a white precipitate with the free acid, or with the salts on the addition of acetic acid. This is an important distinction from the ortho- and pyro-acids.

3. Neither $(NH_4)_2MoO_4$ nor magnesia mixture produces a precipitate. Should one form with the latter reagent, it will readily dissolve on the addition of more NH_4Cl.

4. $BaCl_2$ forms a white precipitate of **barium metaphosphate**, $Ba(PO_3)_2$, soluble in HCl.

5. Metaphosphoric acid upon boiling its solution takes up water and changes to orthophosphoric HNO_3 promotes the change.

REACTIONS OF SOLUBLE SALTS OF BORIC ACID.

Use a 5-per-cent. solution of sodium borate, $Na_2B_4O_7.10H_2O$.

1. $AgNO_3$ produces a white precipitate of **silver metaborate**, $AgBO_2$, soluble in HNO_3 or NH_4OH.

2. $BaCl_2$ precipitates white **barium metaborate**, $Ba(BO_2)_2$, soluble in excess of H_2O, in NH_4Cl or HCl.

3. H_2SO_4 or HCl causes the separation of **boric acid**, H_3BO_3, in crystalline form from strong solutions.

4. Alcohol added to the acid, and ignited, burns with a characteristic **green flame.** In the case of the salts of boric acid, the addition of alcohol is preceded by that of a few drops of H_2SO_4, in order to liberate the free acid. This test is most successful when the acid and alcohol are added to the dry salt and not to the solution; when dissolved in water, the dry salt may be obtained by evaporating to dryness a portion of the solution under examination. Salts of copper when present should be removed before this test is applied, as they likewise impart a green color to the alcohol flame.

REACTIONS OF SOLUBLE SALTS OF CARBONIC ACID.

Use a 5-per-cent. solution of sodium carbonate, $Na_2CO_3 . 10H_2O$.

1. All free acids, except HCN and H_2S, decompose carbonates with effervescence due to the escaping CO_2; the latter passed into a solution of $Ba(OH)_2$ or $Ca(OH)_2$ causes a white precipitate.

2. $BaCl_2$ precipitates white **barium carbonate,** $BaCO_3$, soluble in HCl.

3. $CaCl_2$ produces a white precipitate of **calcium carbonate,** $CaCO_3$, soluble in HCl or $HC_2H_3O_2$.

REACTIONS OF SOLUBLE SALTS OF SILICIC ACID.

Use a 5-per-cent. solution of sodium silicate, Na_4SiO_4.

1. HCl causes in solutions of silicates a gelatinous precipitate of **silicic acid,** H_4SiO_4. On evaporating the mixture with some excess of HCl to dryness and treating the residue with water, finely divided, white **silica,** SiO_2, is obtained.

2. NH_4Cl also precipitates H_4SiO_4 when added to a soluble silicate.

3. Insoluble silicates are determined by fusing on platinum foil some of the fine powder with Na_2CO_3, treating the fused mass with water and HCl, and evaporating to dryness; upon treating the residue with water SiO_2 is left undissolved.

4. Before the blowpipe, with a bead of microcosmic salt ($NaNH_4HPO_4$), silica forms the so-called **silica skeleton,** so characteristic of it.

HYDROFERROCYANIC AND HYDROFERRICYANIC ACIDS.

These acids have been characterized under the reactions of salts of iron, towards which the behavior of their salts is noted. When these compounds are heated with sulphuric acid, **hydrocyanic acid,** HCN, is evolved.

DIRECTIONS FOR THE DETECTION OF THE ACIDS IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP II.

Test the reaction of the original solution with litmus paper; if alkaline, carbonates, borates, and phosphates may be present. If the solution is acid, neutralize with NaOH before applying, to separate portions, the following tests:

I. Add some strong H_2SO_4; an odor of SO_2 alone indicates H_2SO_3. When a precipitate of S accompanies the evolution of SO_2, $H_2S_2O_3$ is present, and H_2SO_3 may be; in such a case, to detect H_2SO_3, apply the next test.

II. Add to some of the original solution $ZnSO_4$; if a precipitate is produced, add sufficient of the reagent to completely precipitate the solution, then add a few drops of $Na_2Fe(NO)(CN)_5$, and finally, after mixing, some $K_4Fe(CN)_6$. A red color results if H_2SO_3 is present.

III. Acidify with HCl and add $BaCl_2$; a white precipitate indicates H_2SO_4.

IV. Add an equal volume of strong H_2SO_4 and some copper turnings, boil; red fumes reveal the presence of HNO_3. Confirm this test by the other reactions of HNO_3.

V. Evaporate a portion of the original solution to dryness, add a few drops of strong H_2SO_4, stir it well through the residue, add 15 to 20 drops of alcohol, and ignite. In the absence of copper, a green flame is evidence of H_3BO_3.

VI. Add $HC_2H_3O_2$ or diluted H_2SO_4 to a portion. An effervescence in the cold without odor indicates H_2CO_3. When other gases are given off at the same time, the CO_2 may be identified by passing it into lime water, with which it produces a white precipitate of $CaCO_3$.

VII. Evaporate a few drops to dryness with HNO_3, dissolve the residue in HNO_3, add the solution to a relatively large quantity of $(NH_4)_2MoO_4$, and warm the mixture gently; a yellow precipitate is obtained if H_3PO_4 is present.

The other acids of this group may be identified as follows:

HClO gives with HCl the odor of Cl. It also produces a white precipitate with $AgNO_3$.

$HClO_3$ evolves Cl upon the addition of HCl, but does not precipitate $AgNO_3$ until it has been heated to redness. Chlorates deflagrate with charcoal.

H_2S is liberated upon the addition of H_2SO_4 and the application of heat. It is recognized by its odor or its action on paper moistened with solution of $Pb(\bar{A})_2$.

HPH_2O_2 is indicated by the odor of H_3P upon strong ignition.

H_4SiO_4 is precipitated as a gelatinous mass when HCl is added to a soluble silicate. To fully confirm this reaction prepare a silica skeleton.

$H_4Fe(CN)_6$ evolves HCN when H_2SO_4 is added and the mixture warmed. Fe_2Cl_6 produces a deep blue precipitate.

$H_6Fe_2(CN)_{12}$ also yields HCN upon treatment with H_2SO_4. It, however, is distinguished from $H_4Fe(CN)_6$ by giving a deep blue precipitate with $FeSO_4$.

$H_4P_2O_7$ causes a white precipitate with $AgNO_3$. By boiling its solution with HNO_3 it is converted into H_3PO_4, which is identified by $(NH_4)_2MoO_4$.

HPO_3 likewise affords a white precipitate with $AgNO_3$. It is changed into H_3PO_4, as is $H_4P_2O_7$; from the latter, however, it differs by producing a precipitate with albumen.

Group III. Acetic Acid, Valerianic Acid, Stearic Acid, Oleic Acid, Lactic Acid, Oxalic Acid, Succinic Acid, Malic Acid, Tartaric Acid, Citric Acid, Carbolic Acid, Benzoic Acid, Salicylic Acid, Gallic Acid, Tannic Acid.

REACTIONS OF SOLUBLE SALTS OF ACETIC ACID.

Use a 2-per-cent. solution of sodium acetate, $NaC_2H_3O_2.3H_2O$.

1. When free, acetic acid is readily recognized by its odor.

2. H_2SO_4, added to an acetate and the mixture warmed, liberates **acetic acid**, $HC_2H_3O_2$.

3. H_2SO_4 and C_2H_5OH in equal volumes, added to an acetate and the mixture warmed, form **acetic ether**, $C_2H_5C_2H_3O_2$, which has a fragrant, slightly acetous odor.

4. Fe_2Cl_6, with a neutral acetate, produces a deep red color, due to **ferric acetate**, $Fe_2(C_2H_3O_2)_6$. This differs from $Fe_2(CNS)_6$ by not being destroyed by $HgCl_2$. Formic acid, $HCHO_2$, also gives a red color with Fe_2Cl_6; but it differs from $HC_2H_3O_2$ by reducing $HgCl_2$ to Hg_2Cl_2 when warmed with the former.

VALERIANIC ACID, $HC_5H_9O_2$.

The odor is sufficient evidence of the presence of this acid. This odor is developed by moisture and heat, and in the case of the salts by the addition of H_2SO_4.

STEARIC ACID, $HC_{18}H_{35}O_2$.

Stearic acid is a white, fatty solid, melting at 69.2° C., giving when combined with potassium a soft soap, and with sodium a hard soap; from both it separates as an oily liquid on the addition of HCl, becoming solid on cooling. Lead stearate, $Pb(C_{18}H_{35}O_2)_2$, is insoluble in ether.

OLEIC ACID, $HC_{18}H_{33}O_2$.

Oleic acid is an oily liquid at ordinary temperatures, but becomes solid at 4° C., and remains so until the temperature rises to 14° C., when it again becomes liquid. Lead oleate, $Pb(C_{18}H_{33}O_2)_2$, prepared by saturating sodium oleate with acetic acid and adding lead acetate, is almost entirely soluble in ether. This is an important distinction from stearic acid.

LACTIC ACID, $HC_3H_5O_3$.

Lactic acid is a colorless, odorless, syrupy liquid which has a very sour taste. It is soluble in water, alcohol, and ether, but insoluble in chloroform. When heated with an equal volume of H_2SO_4 and a few crystals of potassium permanganate, a perceptible odor of aldehyde is obtained. Lactates are all soluble in water, though most of them sparingly; they are insoluble in ether.

Sarcolactic acid, an isomer of ordinary lactic acid, is distinguished from the latter by giving a blue precipitate with copper sulphate.

REACTIONS OF SOLUBLE SALTS OF OXALIC ACID.

Use a 4-per-cent. solution of ammonium oxalate, $(NH_4)_2C_2O_4.H_2O$.

1. $K_2Mn_2O_8$, when added to the solution acidified with H_2SO_4, is decolorized. For the reaction see page 152.

2. $BaCl_2$ produces a white precipitate of **barium oxalate**, BaC_2O_4, sparingly soluble in $HC_2H_3O_2$ or $H_2C_2O_4$, and freely soluble in HCl, HNO_3, or NH_4Cl.

3. $AgNO_3$ precipitates white **silver oxalate**, $Ag_2C_2O_4$, soluble in hot concentrated HNO_3 and in NH_4OH.

4. $CaCl_2$ produces, even in highly dilute solutions, a white precipitate of **calcium oxalate**, CaC_2O_4, soluble in HCl or HNO_3, but insoluble in $HC_2H_3O_2$.

5. $FeSO_4$, with dilute solutions, causes a yellow color; more concentrated solutions yield, upon warming, a yellow precipitate of **ferrous oxalate**, FeC_2O_4. This compound is insoluble in $HC_2H_3O_2$, but dissolves in HCl or HNO_3.

SUCCINIC ACID, $H_2C_4H_4O_4$.

1. $BaCl_2$ produces no precipitate with a solution of a succinate until alcohol is added, when **barium succinate**, $BaC_4H_4O_4$, which is soluble in NH_4Cl, is thrown down.

2. Fe_2Cl_6 causes a brownish-red, bulky precipitate of **ferric succinate**, $Fe_2(C_4H_4O_4)_3$.

3. $Pb(C_2H_3O_2)_2$ precipitates white, amorphous **lead succinate**, $PbC_4H_4O_4$, soluble in HNO_3.

MALIC ACID, $H_2C_4H_4O_5$.

1. $CaCl_2$ fails to give a precipitate with the acid or its salts until the mixture is boiled, when **calcium malate**, $CaC_4H_4O_5.H_2O$, separates. The addition of alcohol will cause this precipitation without boiling.

2. $Pb(C_2H_3O_2)_2$ precipitates white **lead malate**, $PbC_4H_4O_5.3H_2O$.

REACTIONS OF SOLUBLE SALTS OF TARTARIC ACID.

Use a 2-per-cent. solution of potassium and sodium tartrate, $KNaC_4H_4O_6.4H_2O$.

1. $BaCl_2$ precipitates white **barium tartrate**, $BaC_4H_4O_6$, soluble in ammonium salts or in HCl.

2. $CaCl_2$ produces a white precipitate of **calcium tartrate**, $CaC_4H_4O_6.4H_2O$. Ammonium salts prevent this precipitation. The precipitate is soluble in KOH, from which, upon boiling, it is redeposited. $HC_2H_3O_2$ also dissolves $CaC_4H_4O_6.4H_2O$.

3. $AgNO_3$ causes a white precipitate of **silver tartrate**, $Ag_2C_4H_4O_6$, which becomes black on boiling, owing to the separation of metallic **silver**, Ag. If, however, the precipitate be dissolved in a few drops of NH_4OH, and the solution so obtained be boiled, a mirror of Ag forms on the test-tube. The vessel must be perfectly cleaned for this reaction; to accomplish this, rinse it with KOH solution and then thoroughly with water.

4. $Ca(OH)_2$ in excess causes a precipitate of **calcium tartrate**, $CaC_4H_4O_6.4H_2O$. This precipitate is flocculent at first, in which state it is readily soluble in NH_4Cl, but after standing for some time it becomes crystalline; it is then insoluble in NH_4Cl.

5. $H_2C_4H_4O_6$ and tartrates char on heating, and with H_2SO_4 the odor of burnt sugar is given off.

REACTIONS OF SOLUBLE SALTS OF CITRIC ACID.

Use a 2-per-cent. solution of potassium citrate, $K_3C_6H_5O_7.H_2O$.

1. $BaCl_2$ produces a white precipitate of **barium citrate**, $Ba_3(C_6H_5O_7)_2$, soluble in excess of water, in ammonium salts, or in acids.

2. $CaCl_2$ precipitates white **calcium citrate**, $Ca_3(C_6H_5O_7)_2$, when the solutions are boiled together. The precipitate is much more soluble in cold water; it is also soluble in cold NH_4Cl, but redeposited upon boiling. KOH does not dissolve it.

3. $AgNO_3$ produces a white precipitate of **silver citrate**, $Ag_3C_6H_5O_7$; on boiling no metallic mirror is formed.

4. $Ca(OH)_2$, in excess, does not cause a precipitate until the mixture is boiled. This is an important distinction from tartaric acid.

5. $H_3C_6H_5O_7.H_2O$ and citrates char on heating, and with H_2SO_4 give off the odor of burnt sugar.

Carbolic Acid, C_6H_5OH.

1. HNO_3, with an aqueous solution of the acid, forms a yellow color, due to the formation of **picric acid**, $C_6H_2(NO_2)_3OH$.

2. Fe_2Cl_6 produces a **violet-blue** color.

3. A piece of pine wood dipped in the acid and then exposed to the fumes of HCl becomes, after a short time, colored **blue**.

4. Bromine water causes a white precipitate of **tribromphenol**, $C_6H_2Br_3OH$, which, under the microscope, appears crystalline.

5. Albumen or collodion is **coagulated** by carbolic acid.

Reactions of Benzoic Acid, $HC_7H_5O_2$.

1. Fe_2Cl_6 precipitates from neutral solutions flesh-colored **ferric benzoate**, $Fe_2(C_7H_5O_2)_6$, decomposable by HCl with the separation of $HC_7H_5O_2$.

2. HCl causes the separation of $HC_7H_5O_2$ from cold solutions of the benzoates.

3. $BaCl_2$ and $CaCl_2$ produce no precipitates with either the free acid or its salts.

4. $HC_7H_5O_2$ is soluble in petroleum ether; the latter solvent removes the acid from its aqueous solution when agitated therewith.

5. Heated in a test-tube with freshly slaked lime, benzoic acid yields **benzol**, C_6H_6, recognizable by its odor.

6. The pure acid melts at 121.4°.

Reactions of Salicylic Acid, $HC_7H_5O_3$.

1. Fe_2Cl_6 produces a deep **violet** color, which is very characteristic.

2. Warmed with H_2SO_4 and CH_3OH, the fragrant odor of **methyl salicylate**, $CH_3C_7H_5O_3$, is developed.

3. HCl causes the separation of $HC_7H_5O_3$ from cold solutions of the salicylates.

4. $HC_7H_5O_3$ is insoluble in petroleum ether. Advantage is taken of this fact to separate benzoic and salicylic acids when mixed.

5. The pure acid melts at 156° to 157°.

CINNAMIC ACID, $HC_9H_7O_2$.

Cinnamic acid crystallizes in prisms which melt at 133° C., and boil at 300° C. It is difficultly soluble in water, more readily in alcohol, and easily in ether. It can be sublimed, and is volatile in a current of steam. HCl causes the separation of $HC_9H_7O_2$ from cold solutions of the cinnamates. Oxidizing agents, like potassium permanganate, convert cinnamic acid into benzaldehyde, which may be recognized by its odor of bitter almonds.

REACTIONS OF GALLIC ACID, $HC_7H_5O_5.H_2O$.

1. $FeSO_4$ causes no change in color.

2. Fe_2Cl_6 produces a bluish-black precipitate, which disappears on heating.

3. KOH or NaOH, if not in excess, develops slowly a deep green color, which becomes red on the addition of acids. Alkali carbonates cause the same green color, although more slowly.

4. No precipitate is produced with either gelatin or the alkaloids. With the former, however, a precipitation takes place when gum is present.

REACTIONS OF TANNIN.

Tannic Acid, *Gallotannic Acid*, $C_{14}H_{10}O_9$.

1. $FeSO_4$, when perfectly pure, causes no change. In the presence of oxygen, however, a dark color rapidly develops; this, on standing, slowly becomes a precipitate.

2. Fe_2Cl_6 produces a bluish-black precipitate. An excess gives a green color because of the acid usually present in the reagent.

3. $Fe_2(NH_4)_2(SO_4)_4$ affords the same color and precipitate, and, as it contains no free acid, constitutes a better reagent than Fe_2Cl_6.

4. Test solution of iodine mixed with a small quantity of ammonium hydrate, previously diluted with ten times its volume of water, produces a brilliant red color. This reaction will take place with only traces of tannic acid.

5. Gelatin causes a white, flocculent precipitate. This reaction is more delicate in the presence of alum.

6. Alkaloids produce white precipitates, soluble in acetic acid and in alcohol.

7. $K(SbO)C_4H_4O_6$ causes a white, gelatinous precipitate. Most other metallic salts likewise give precipitates.

8. $Ca(OH)_2$ produces a bluish-white precipitate; in large excess, it gives a pinkish tint to the solution.
9. Bromine water gives no precipitate with gallotannic acid.

Oak-Bark Tannin.

1. Ferrous salts cause no change in color.
2. Ferric salts give green color and precipitate.
3. $Ca(OH)_2$ produces a pinkish precipitate, which gradually becomes red and brown.
4. Bromine water gives a yellow precipitate.
5. Gelatin produces a white, flocculent precipitate.

DIRECTIONS FOR THE DETECTION OF THE ACIDS IN A SOLUTION CONTAINING SOLUBLE SALTS OF GROUP III.

As many of the acids in this group would indicate their presence by odor or physical appearance, a method of separating only the more important and closely related ones will be given. The list will, therefore, be limited to Acetic Acid, Oxalic Acid, Tartaric Acid, and Citric Acid.

The solution should be neutral to litmus paper; if acid, neutralize with NaOH, if alkaline, with HNO_3.

To a small portion add an equal volume each of strong H_2SO_4 and C_2H_5OH and warm. Acetic acid will, if present, be indicated by the odor of acetic ether.

Make another portion slightly alkaline with NH_4OH, add $CaCl_2$, allow to stand (avoiding heat) for ten minutes, and filter (make sure the precipitation has been complete).

Ppt. $H_2C_2O_4$. $H_2C_4H_4O_6$. Wash, pour on the filter $HC_2H_3O_2$.		**Filt. $H_3C_6H_5O_7$.** Boil to expel all NH_4OH. White ppt. slowly forming on the sides of the tube indicates $H_3C_6H_5O_7$.
Ppt. $H_2C_2O_4$. Confirm by testing the original solution with $HC_2H_3O_2$ and $CaCl_2$.	**Filt. $H_2C_4H_4O_6$.** Add NH_4OH until slightly alkaline. White ppt. Confirm by forming mirror with $AgNO_3$ in original solution.	

CHAPTER IV.

THE DETECTION OF BASES AND ACIDS.

SPECIAL OBSERVATIONS.

THE bases must always be determined first in a portion of the solution or powder, according to chart, page 47.

Besides the substances mentioned in the precautions on page 46, certain acids, when present in combination, as, for instance, benzoic and salicylic, are also precipitated from their salts by HCl; in such cases it is first necessary to evaporate the solution to dryness and heat to redness before proceeding with the detection of bases.

The chart on page 66 must be used in the analysis of the precipitate of Group IV., when the latter is mixed with the phosphates of Ba, Sr, Ca, and Mg (determined by dissolving a small portion of the precipitate in a few drops of HNO_3 and testing with $(NH_4)_2MoO_4$). The addition of Na_2HPO_4 is to insure the formation of the phosphates of Fe, Ce, Al, Cr, and Mn. The $NH_4C_2H_3O_2$ should be freshly prepared by adding $HC_2H_3O_2$ to NH_4OH until the solution is slightly acid; it is used to neutralize the HCl with liberation of $HC_2H_3O_2$. The presence of oxalates would likewise necessitate an exception to the general chart for the detection of bases; when present, therefore, the substance must be heated to redness before commencing the analysis.

When the analysis of a solid is to be performed, all of its physical properties should be carefully observed. The action on litmus paper of any portion soluble in water is also to be noted, and the solution made neutral if necessary.

If only the alkali metals are present and the reaction is neutral, proceed to search for the acids according to Division I. If the reaction is acid or alkaline, neutralize as directed in Division II.

If other than the alkali metals are present, and the reaction is acid, conduct the detection of the acids according to Division II.

When the substance is not entirely dissolved by H_2O, HCl, or a mixture of HCl and HNO_3, proceed for both bases and acids according to Division III.

CHART FOR THE ANALYSIS OF THE PRECIPITATE OF GROUP IV. WHEN PHOSPHATES ARE PRESENT.

<table>
<tr><td colspan="6">Dissolve the precipitate in HCl, add Na_2HPO_4, then excess of $NH_4C_2H_3O_2$, boil, and filter.</td></tr>
<tr><td colspan="2">Ppt. Fe, Ce, Al.
Wash with hot H_2O, then pour on the filter hot solution of KOH.</td><td colspan="4">Filt. Ba, Sr, Ca, Mn, Mg, Cr (Green, if Cr be present).
Add K_2CrO_4, warm, and filter.</td></tr>
<tr><td rowspan="2">Ppt. Fe, Ce.
Wash, dissolve in HCl. Test a portion with $K_4Fe(CN)_6$ for Fe(ic).
Blue ppt.
Confirm in original solution.</td><td rowspan="3">Filt. Al.
Acidify with $HC_2H_3O_2$.
White ppt.</td><td rowspan="3">Ppt. Ba.
Yellow.</td><td colspan="3">Filt. Sr, Ca, Mn, Mg.
Add very dilute H_2SO_4, allow to stand, filter. An excess of H_2SO_4 should be avoided.</td></tr>
<tr><td rowspan="2">Ppt. Sr.
White. Confirm by flame test.</td><td colspan="2">Filt. Ca, Mn, Mg.
Add $NH_4C_2H_3O_2$ and $(NH_4)_2C_2O_4$, filter.</td></tr>
<tr><td>To another portion add $H_3C_6H_5O_7$, NH_4OH in excess, and Na_2HPO_4.
White ppt. indicates Ce.</td><td>Ppt. Ca.
White.</td><td>Filt. Mn, Mg.
Apply Crum's test for Mn to the original solution. To the remaining portion add Fe_2Cl_6, filter out the $Fe_2(PO_4)_2$, to the filtrate add NH_4Cl, NH_4OH, and NH_4HS, to remove Fe, Cr, and Mn, filter, and test filtrate with Na_2HPO_4.
White, crystalline ppt. indicates Mg.</td></tr>
</table>

DIVISION I. When the bases are the alkali metals, and the reaction of the solution is neutral.

RULE I.—*Evaporate a portion of the solution to dryness and slowly heat to redness.*

If the mass char, one or more of the following salts of organic acids are indicated: **Acetates, Lactates, Succinates, Malates, Tartrates, Citrates, Benzoates, Salicylates, Gallates, Tannates. Oxalates** do not char, although if the heating take place slowly a grayish coloration may be noticed. The residues in all these cases give off CO_2 on the addition of H_2SO_4.

Fe_2Cl_6, applied to the original solution, usually detects **Benzoates, Salicylates, Gallates,** and **Tannates.** When unmixed, the color obtained will distinguish the first two. Benzoic and salicylic acids are precipitated upon acidifying the solution. They may be removed from their water solution by shaking with ether, and afterwards separated by the use of petroleum ether; both the soluble and insoluble portions should then be further tested with the reagents given under the reactions of these acids. Gallic and gallotannic acids give with Fe_2Cl_6 precipitates of the same color. Upon agitating the water solution with ether, gallic acid is dissolved, and, upon separating and evaporating the solvent, may be identified by the usual reagents for that acid.

Tannic acid differs from gallic acid by being more soluble in water, and by this solution producing a precipitate with gelatin.

The detection of the organic acids of more common occurrence is conducted according to the chart on page 64.

The physical properties of the salts of the other organic acids will usually aid in their recognition by the tests given in the consideration of them.

Rule II.—*Evaporate another portion to dryness, allow the residue to cool, add a few drops of strong* H_2SO_4, *warm gently, and note any of the following effects which may ensue from this single reaction:*

Effervescence in the cold, no odor	Carbonates.	Confirm in original solution by dilute acid.
Effervescence on heating, odor of H_2S	Sulphides	Confirm by adding acid to original solution.
Odor of SO_2	Sulphites	
Odor of SO_2 with separation of S	Thiosulphates	
Dark-brown color and violet fumes	Iodides.	Confirm by starch and Cl water.
Dark-red color and reddish fumes	Bromides.	Confirm by starch and Cl water.
Odor of HCN	Cyanides, Ferro- or Ferri-Cyanides.	Confirm in original solution.
Odor of $HC_2H_3O_2$	Acetates.	Confirm by acetic ether test.
Odor of Cl	Hypochlorites.	
Odor of Cl_2O_4	Chlorates.	
Strongly acid suffocating fumes	Chlorides.	Confirm by $AgNO_3$.
Strongly acid fumes, odor of N_2O_4	Nitrates.	Confirm by other tests.
Characteristic odors	Benzoates, Succinates, Valerianates, Carbolates, Hypophosphites.	

RULE III.—*Acidify a third portion with* HCl *and add* $BaCl_2$.
A white precipitate indicates **Sulphates.**

RULE IV.—*To a fourth portion add* $CaCl_2$.

A white precipitate soluble in excess of H_2O indicates **Sulphates**; if insoluble in excess of H_2O or $HC_2H_3O_2$, **Oxalates** are indicated. A white precipitate, soluble in KOH and reprecipitated upon boiling, indicates **Tartrates**; the latter test should be confirmed by forming a mirror of silver on the test-tube. A white precipitate, soluble in NH_4Cl and reprecipitated upon boiling, indicates **Citrates.**

For further instruction regarding the separation of these acids consult the chart on page 64.

When **Sulphates** are present it is important to remove them before attempting the detection of **Oxalates, Tartrates,** and **Citrates** by the use of $CaCl_2$. To accomplish this, treat the solution with HCl and $BaCl_2$, filter off the $BaSO_4$, neutralize the filtrate with NaOH, and proceed according to the chart on page 64.

RULE V.—*Acidify a fifth portion with* HNO_3 *and add* $AgNO_3$ *until the precipitation is completed.*

Collect the precipitate, wash it, and pour upon the filter NH_4OH. Acidify the filtrate so obtained with HNO_3; a white precipitate indicates **Chlorides.** When **Cyanides** are present they must be removed by boiling with HNO_3 before adding the $AgNO_3$.

RULE VI.—*Add to a sixth portion of the solution starch paste and chlorine water.*

A blue color indicates **Iodides.** Continue the addition of chlorine water until the blue color of starch iodide is discharged, then shake with chloroform. A yellowish-red color is imparted to this solvent if **Bromides** are present.

For fuller directions, see page 50.

RULE VII.—*Add a few drops of the solution to a relatively large quantity of* $(NH_4)_2MoO_4$ *and warm.*

Phosphates and **Arsenates** produce yellow precipitates. The presence or absence of As is always ascertained in the detection of bases. When present, it should be separated from another portion of the solution by HCl and H_2S; the filtrate, after boiling to expel H_2S, is then neutralized with NH_4OH and treated with magnesia mixture. A white crystalline precipitate confirms the presence of **Phosphates.**

The detection of **Pyrophosphates** and **Metaphosphates** may be conducted by the directions given on page 59.

RULE VIII.—*To an eighth portion apply the special test with* H_2SO_4 *and* $FeSO_4$ *for* **Nitrates.**

A dark layer at the line of contact reveals their presence.

RULE IX.—*To some of the dry salt, or to the residue obtained by evaporating a portion of the solution to dryness, add a few drops of strong* H_2SO_4 *and 15 or 20 drops of alcohol, mix well, and apply flame.* **Borates,** *if present, will impart a green color to the flame of the burning alcohol.*

Chromates, Manganates, and **Permanganates,** when present, impart color to the solution. The metals from which their acid radicals arise will be ascertained in the detection of bases. The characters of these salts have been previously discussed under different reactions, which may be employed to more fully establish the presence of their constituent acids.

DIVISION II. When the solution is acid to litmus paper, or when the substance to be analyzed is a solid which requires the use of acid to dissolve it.

Test portions of the material according to Rules I. and II., **DIVISION I.** *Then determine the bases in another portion by the chart on page 47 (bearing in mind the exception in regard to phosphates).*

Another portion of the material is then to be treated as follows:

<table>
<tr><td colspan="3">Boil with enough solution of Na_2CO_3 to make the mixture alkaline, filter.</td></tr>
<tr><td rowspan="2">Ppt. consists of the carbonates, hydrates, and oxides of the bases present, and is disregarded.</td><td colspan="2">Filt. contains the acids in the form of salts of Na. Divide into two portions.</td></tr>
<tr><td>To one portion add HCl until slightly acid, boil to remove CO_2, neutralize with NaOH, and test according to Rules III, IV, VI, VIII, and IX, DIVISION I.</td><td>To another portion add HNO_3 until slightly acid, boil to remove CO_2, neutralize with NaOH, and test according to Rules V and VII, and if necessary III, IV, VI, and IX, DIVISION I.</td></tr>
</table>

When heavy metals are present Rule I, Division I, is preferably applied to the filtrate after boiling with Na_2CO_3; the portion neutralized with HCl and NaOH is recommended for use in all such cases. Rule II. should be invariably performed on the original solution or solid. When Cu is present it is best to add, along with the Na_2CO_3, some NaOH to insure the complete precipitation of that base.

HYDRATES, OXIDES, AND METALS.

When, in the analysis of an inorganic substance for acids, negative results are obtained, the material under consideration may be either a hydrate, an oxide, or a metal.

The hydrates of K, Na, Li, Ca, Sr, and Ba are soluble in water, and yield solutions which change red litmus paper blue. The hydrates of other metals are insoluble in water. These, as also the hydrates of Ca, Sr, and Ba, when heated in a dry test-tube, give off vapor of water which condenses on the cooler part of the tube; it is characterized by having no odor or taste, and by not changing the color of litmus paper.

Oxides do not yield water when thus heated. The oxides of K, Na, Li, Ca, Sr, and Ba dissolve in water to form hydrates. The oxides of other metals are insoluble in water, but dissolve in acids without effervescence.

The free metals may be recognized by their general physical properties. Some of them cause an evolution of hydrogen when treated with dilute hydrochloric or sulphuric acids.

DIVISION III. When the substance is not entirely dissolved by H_2O, HCl, or a mixture of HCl and HNO_3.

To ascertain if any part of the substance is soluble, add a small portion of it to some water; if all of it does not pass into solution, filter and evaporate a small quantity of the filtrate to dryness to see if the liquid contains solid matter. If a residue is obtained in the dish, the substance is at least partly soluble in water, and the solution should be examined for bases by the chart on page 47, and for acids by Division I. If the substance is not entirely soluble in water, boil the part insoluble in water with HCl, or, if necessary, with a mixture of HCl and HNO_3. Analyze any substance these may dissolve for bases by the chart on page 47, and determine the acids according to Division II. An insoluble residue may consist of one or more of the following substances: Sulphates of Ba, Sr, Ca, Pb; Chlorides, Bromides, and Iodides of Ag, Pb; certain Oxides which have been highly heated, as Fe_2O_3, Al_2O_3, Cr_2O_3, SnO_2; Silica and Silicates; Carbon and Sulphur (the last two are readily detected in the preliminary examination by heat). This residue is mixed with about four times its weight of dry Na_2CO_3, and fused on a platinum foil; the mass is boiled with water, and the soluble portion examined for acids according to Division II. The portion undissolved by water is treated with HCl; the solution so obtained evaporated to dryness, the residue dissolved in water with the aid of a little HCl, and examined for bases by the chart on page 47. Special attention should be given to the notes preceding this chart. If, after fusing with Na_2CO_3, the metals lead and silver are present in the residue insoluble in water, they can best be determined by dissolving in HNO_3 and proceeding with the analysis as directed in Division II. Many of these insoluble substances can be detected in a preliminary examination by the use of the blowpipe, as explained in the reactions given under the individual elements.

THE ANALYSIS OF METALS AND ALLOYS.

The following general outline suffices for the examination of the more common metals and alloys:

Pour over the substance HNO_3, sp. gr. 1.20, and evaporate to dryness with a moderate heat. This treatment converts most of the metals into nitrates, which are soluble in water or very weak HNO_3; Sb and Sn are, however, changed to oxides, which are insoluble in water or HNO_3, while Pt and Au remain unaltered in the metallic state, and hence fail to dissolve in the same liquids.

The residue obtained upon evaporating to dryness is treated with water containing a small amount of HNO_3 to insure the solution of bismuth; the mixture is then filtered, and the analysis of the filtrate conducted according to the chart on page 859. The oxides of Sb and Sn may be separated from the metallic Pt and Au by warming with strong HCl; after filtration the Sb and Sn are separated by the chart on page 35.

Pt and Au may be identified by dissolving in a mixture of HCl and HNO_3, and applying the tests given in the chart on page 35.

PART II.

QUANTITATIVE ANALYSIS.

CHAPTER I.

GRAVIMETRIC PROCESSES.

PRELIMINARY CONSIDERATIONS.

THE object of quantitative analysis is the determination of the amount of any given substance. It must always be preceded by qualitative analysis, which determines the nature of the material under examination and indicates the methods which may be employed for its estimation. Therefore, previous to undertaking this section the student should be thoroughly familiar with the preceding qualitative operations. Gravimetric analysis is that division of quantitative analysis which ascertains the quantity of a substance by converting it into a compound of definite composition and accurately weighing this compound; from the weight of the latter the quantity of the original substance is then found by calculation.

In the following course in gravimetric analysis some typical methods of estimation are given as examples for practice, with the belief that a thorough knowledge of the operations involved in these will enable the learner to carry out most of the gravimetric processes he will be called on to perform in inorganic work. That the student may conscientiously satisfy himself of his ability to conduct such chemical processes, it will be well for him to practise each method of estimation until the results of his repeated analyses agree with one another. The methods of analysis given for practice are not always applicable to mixtures, as several substances may be precipitated by the same reagent. The procedure in case of a mixture depends altogether upon the bases and acids present, and in some instances may involve an entirely different method from the one given in the following course for the particular base or acid; but if the student understands qualitative analysis, he will be able to devise a plan of separating the interfering substances or of estimating the several constituents which may be present in a mixture.

If not already in a state of uniform division, the sample of the substance to be estimated should always be brought into that condition and thoroughly mixed, so that the portion taken for analysis will be representative of the entire lot.

The first step in every quantitative analysis is the weighing of a portion of the material to be analyzed. No fixed quantity can be prescribed as suitable in every case, although from 0.5 to 1 gramme of the ordinary compounds of the bases and acids dealt with in this course will usually suffice for a single determination.

It is especially desirable at this point that the student should have instruction from some one familiar with the use of analytical balances and weights. In addition, the following rules should be kept constantly in mind by those using a fine balance:

1. Never put any chemical substance directly on the pan of a balance, but first weigh a clean, dry crucible or watch crystal, and then weigh the substance in it.

2. Never put on or take off a weight, or anything else, from a balance when the beam is resting on the knife-edges.

3. All weights should be transferred in regular order, and the forceps always used instead of the fingers.

4. Volatile acids, and all other corrosive substances, like chlorine water, iodine, or solution of ammonia, as well as hygroscopic substances, should be weighed in stoppered weighing-tubes or small test-tubes with closely fitting corks.

5. The door of the balance should be kept open no longer than is absolutely necessary.

In addition to the above rules, it may be said that substances and containers, that are heated previous to weighing, should be cooled in a desiccator before being put on the balance-pan.

Before beginning quantitative operations the student should provide himself with a note-book, to be used for this purpose only, and in which he should keep a record of all weighings in a systematic manner, so that they may be referred to on short notice.

Precipitation.—When a substance has been weighed it is usually first dissolved, the solvent and the manner of applying it depending on the nature of the material under investigation. Solution is generally followed by precipitation, which should be conducted in beaker glasses, or, in a few cases, when an alkaline liquid is to be boiled, for instance, in porcelain evaporating dishes.

If the mixture is to be boiled during precipitation, it should be stirred to prevent loss of material through bumping.

The reagent to be added should be in clear solution, and should be gradually added and thoroughly mixed through the solution to be precipitated; a large excess of the reagent should be avoided, except in a few cases where it is especially directed. The filtrate should always be tested with a few more drops of the reagent to determine whether the precipitation has been completed.

Distilled water should be employed in all quantitative operations.

Filtration.—Filter paper having a very small ash should be employed. That known in commerce as Swedish No. 2 will be found satisfactory for most purposes.

Plain filters should always be used. They are made by folding a circular piece of the paper twice, and then opening so as to form a cone, which will exactly fit into a 60° funnel, so that the liquid will pass out at the point of the cone, instead of escaping at the sides. By this means a precipitate can be more thoroughly washed, and in a shorter time.

The filter should be of such size that it will not project above the edge of the funnel.

Balanced filters are usually used to collect precipitates which are to be dried and weighed without ignition. These are made by trimming the edge of the heavier of two filters with scissors until the two sheets exactly counterpoise each other, when one is put on each pan of the balance. To use balanced filters in collecting a precipitate, fold them separately as in the case of plain filters, then open each so as to form a cone, and place one within the other in such a way that there will be four thicknesses of the paper all around. In weighing on balanced filters the inner filter containing the precipitate is put on one pan of the balance and the outer filter upon the other pan, then weights are put upon the latter until the loads of the two pans exactly balance. As the filters balance each other, it is obvious that the weights used to bring about an equilibrium show at once the weight of the precipitate.

The precipitate should be allowed to settle in the vessel after it is formed. The clear, supernatant liquid is then to be transferred to a filter by pouring it down a glass rod held against the lip of the beaker to conduct it into the filter without loss.

The precipitate is then washed into the filter with the aid of a jet from a wash-bottle, and the washing continued until, by the appropriate test, it is found to be complete.

The small portions of the precipitate which adhere to the sides of the beaker are removed with a glass rod having on its end a short section of closely fitting rubber tubing.

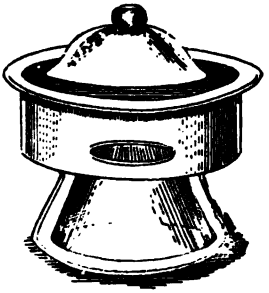
Precipitates which clog the filter, as, for instance, aluminum hydrate, are best washed by decantation. This is accomplished by pouring the wash-water over the precipitate, allowing the latter to settle, then transferring the clear, supernatant liquid to a filter by pouring it down a glass rod as already mentioned, and, finally, when the washing is found to be complete, collecting the precipitate on the filter for drying. The washing in many cases is to be done with hot water; in all cases each portion of the liquid used for washing should be allowed to completely drain through before adding more.

Drying.—The filter and its contents may be dried in the funnel, set in a warm place or an air-bath, or they may be removed from the funnel, placed on a watch crystal or in a crucible, and dried in an air-bath at any suitable temperature. If the precipitate is to be ignited, it should be dried until the filter is no longer moist to the touch. To prove that the drying is complete in cases where the substance is not to be ignited, the substance and its container, after being weighed, are put back into the air-bath, heated for half an hour longer, then allowed to cool, and weighed again; if the weight is found to be unaltered upon the second weighing, the process is known to be at an end. Such a course would be pursued in estimating water of crystallization in salts.

The temperatures given in this book are based upon the Centigrade scale.

Ignition.—This is usually performed in a platinum or porcelain crucible. In the examples given for practice the material of the crucible is specified, in other cases the operator must decide from the character of the material and the treatment to be given it whether a porcelain or platinum crucible should be used. Where the conditions will admit of the use of a platinum crucible it is to be preferred to a porcelain one, on account of the greater ease with which it may be heated and cooled. Metals, metallic compounds which are liable to reduction, the solid non-metals, the halogens (except fluorine), the caustic alkalies, and the cyanides, as well as mixtures which yield any of these substances, should never be ignited in platinum. Alkalies cannot be fused in porcelain crucibles, nor fluorides treated with acids therein. Platinum ware should never be heated in the inner cone of the Bunsen burner flame, as the texture of the metal is injured thereby. Platinum vessels should be supported on platinum or pipe-stem triangles during ignition. They are usually cleaned by rubbing them with moistened sea-sand, or by fusing in them a quantity of acid potassium sulphate until white fumes of sulphur trioxide are evolved, then shaking the fluid around on the sides, allowing the vessel to cool, washing out the salt with water, and burnishing with wet sand. The filter containing the precipitate can be folded, then put into the crucible, and the ignition started; or the precipitate may be separated from the filter, transferred to the crucible, and the filter burned separately. The second method is to be adopted where the precipitate is of such character that it is liable to alteration by the burning paper. To conduct this last method it is best to place the crucible upon a sheet of glazed paper, and then, having loosened as much of the precipitate as possible from the filter by rolling it in the fingers, to carefully transfer the precipitate to the crucible by holding the filter in a slanting position over the crucible and giving the filter a few gentle taps with the fingers. The filter is then folded around the adhering particles in such a way as to completely envelop them, the package finally being made up into a roll, all the time keeping the filter over the sheet of glazed paper. Around this roll a platinum wire is wrapped in the form of a spiral, leaving sufficient length to act as a handle by which to hold the package over the crucible. The paper is then lit by touching it with a Bunsen burner flame, and the carbonized residue of the filter is allowed to drop upon the precipitate in the crucible. Any particles of precipitate or filter ash which may have fallen on the glazed paper are then put in the crucible, and the latter supported on a triangle. Heat is then applied and gradually increased until the whole is brought to dull or bright redness as is required. After from fifteen to thirty minutes' heating the crucible with its contents are removed to a desiccator (Fig. 6) and there allowed to cool until of the temperature of the balance-room, when they are ready for weighing. After being weighed the crucible and contents must always be reignited for a few minutes and again weighed; if the weight is found to have been unchanged by this treatment the ignition has been sufficient. The ash of the filter paper should be deducted from the weight of the contents of the crucible. A good Bunsen burner will usually furnish sufficient heat for the ignitions given in this course, although a blast-lamp will be needed in some special cases, as, for instance, that of calcium oxide. Substances which are affected in undesirable manners when ignited in contact with air may be ignited in hydrogen or carbon dioxide as suits the case. When an ignition is to be done in a current of hydrogen, the gas is generated in the usual way, and, after being passed through a tube filled with calcium chloride to dry it, is conducted into the crucible through an ordinary clay smoking pipe the bowl of which has been inverted over, or within, the crucible. When the hydrogen has been shown to be free from air, the fire may be applied to the crucible. The ignited material must be allowed to cool in the hydrogen before being weighed. Hydrogen sulphide can be substituted for hydrogen in some instances. Finally, in all cases whatsoever, the purity of the weighed material must be proved before the results of analysis are calculated.

FIG. 6.



Desiccator.

Calculation of Results.—The calculations that are needed to find the results of the gravimetric methods given for practice can probably be sufficiently explained by the following illustration:

Suppose we have taken 0.475 gramme of barium chloride, and find 0.455 gramme of barium sulphate, we have:

Molecular Wt. of $BaSO_4$.		Atomic Wt. of Ba.		Wt. of $BaSO_4$ found.		Wt. of Ba found.
232.72	:	136.90	: :	0.455	:	0.267+

Having determined the amount of barium found, we make another proportion in order to calculate the percentage found, that we may compare it with the theoretical percentage in the barium chloride:

Wt. of $BaCl_2.2H_2O$ taken.		Wt. of Ba found.				Per cent. of Ba found.
0.475	:	0.267+	: :	100	:	56.21

The theoretical percentage of barium is ascertained as follows:

Molecular Wt. of $BaCl_2.2H_2O$.		Atomic Wt. of Ba.				Per cent. of Ba.
243.56	:	136.90	: :	100	:	56.21

By substituting for the atomic weight of the barium the molecular weight of the chlorine or of the water in the foregoing proportion the percentage of either of these constituents in barium chloride may be computed.

$$\begin{array}{rcrcrl} \mathrm{Ba} & = & 136.90 & = & 56.21 & \text{per cent.} \\ \mathrm{Cl_2} & = & 70.74 & = & 29.04 & \text{"} \\ \mathrm{2H_2O} & = & \underline{35.92} & = & \underline{14.75} & \text{"} \\ & & 243.56 & & 100.00 & \end{array}$$

SECTION I.

ESTIMATION OF BASIC RADICALS IN SIMPLE SALTS.

ESTIMATION OF POTASSIUM IN POTASSIUM SALTS.

Solution.—All the ordinary compounds of potassium are soluble in water.

Estimation as Potassium Sulphate, K_2SO_4.—The potassium salts of organic and volatile inorganic acids are most conveniently converted into potassium sulphate for estimation. Salts of organic acids should be carbonized in a crucible by a low heat, the mass allowed to cool, some solid ammonium sulphate added, and enough water put into the crucible to dampen the contents. The latter is then carefully heated until dry. After attaining this point the residue is gradually heated to dull redness, until white fumes of ammonium salts cease to be given off, and finally to bright redness. When cool, the crucible and contents are ready for weighing. The estimation of potassium in Rochelle salt and tartar emetic forms exceptions to this method, as the sodium sulphate or antimony tetroxide would be weighed as potassium sulphate. For the method to be adopted in the case of Rochelle salt, see page 80. When potassium is to be estimated in tartar emetic, dissolve the compound and precipitate the antimony in the form of antimonous sulphide, as directed on page 97 ; evaporate the filtrate and washings to dryness, carbonize the residue, treat it with dilute sulphuric acid, evaporate to dryness, and ignite according to the following directions for the estimation of potassium in its salts with volatile inorganic acids.

Potassium sulphate may be had, for weighing, from the salts of potassium with volatile inorganic acids by adding sulphuric acid to the solution of the salt, evaporating to dryness, and igniting the residue. Enough sulphuric acid has been used if white fumes of sulphur trioxide are evolved on ignition. At this stage the residue may consist largely of acid potassium sulphate; to convert it into the normal salt, allow the crucible to cool somewhat, add a small lump of ammonium carbonate, and then heat to dull redness. Normal potassium sulphate is solid at a dull red heat, while the acid sulphate fuses readily at that temperature; the treatment with ammonium carbonate must therefore be repeated, if necessary, to bring about this change in fusibility. When the residue has been completely changed into normal sulphate and fumes of ammonium sulphate no longer issue from the crucible, the latter is brought to bright redness for a few minutes; then, after being allowed to cool, it is weighed.

To estimate potassium in potassium alum, precipitate the aluminum as hydrate, according to the directions given for the estimation of aluminum on page 93, filter, evaporate the filtrate and washings to dryness, ignite to expel ammonium sulphate, and weigh the residue as potassium sulphate.

Estimation as Potassium Platinic Chloride, K_2PtCl_6.—This method is applicable to all potassium salts of acids soluble in alcohol. In the case of salts of volatile acids the following course is usually pursued:

A weighed quantity of the salt (about 0.050 to 0.075 gm.) is dissolved in a little water, hydrochloric acid is added, and the mixture is carefully evaporated to dryness. The residue is dissolved in a small amount of water with a few drops of hydrochloric acid, and solution of platinic chloride is added. The mixture is carefully evaporated nearly to dryness over a water-bath, keeping the water in the bath just below the boiling point. The residue is treated with 80 per cent. (by volume) alcohol.*

If the alcohol does not acquire a yellow color, too little platinic chloride has been added, in which event the alcohol is carefully evaporated, more platinic chloride added, the evaporation therewith repeated, and the residue treated again with 80 per cent. alcohol. If the alcohol is colored yellow, the mixture is allowed to stand some hours. At the expiration of this time the precipitate is collected on a small balanced filter and washed with 80 per cent. alcohol until the washings are colorless.

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* Rules for making an alcohol of any required lower percentage from an alcohol of any given higher percentage will be found on page 317.

The filters and contents are then carefully dried at a low heat, the temperature being afterwards raised to 130°, and the drying continued at that point till the weight is constant.

When a potassium salt of a non-volatile acid is to be operated on, the salt is dissolved in a small quantity of water, a few drops of hydrochloric acid added, then platinic chloride in excess, and this followed with several volumes of strong alcohol. The mixture is allowed to stand twenty-four hours, then the precipitate is collected, washed, dried, and weighed, as already stated.

To determine potassium in Rochelle salt, first carefully carbonize the salt, then ignite until the carbon is consumed, allow the crucible to cool, treat its contents with an excess of ammonium chloride in solution, evaporate to dryness, heat to expel ammonium salts, finally to incipient fusion, allow to cool, and weigh the residue of potassium and sodium chlorides. Determine the potassium in this residue as potassium platinic chloride by the directions given on page 79.

Potassium chromate, bichromate, ferricyanide, ferrocyanide, and permanganate cannot well be analyzed for potassium by the foregoing methods; but these, however, are valued more for their acid radicals than for the potassium they may contain. The estimation of potassium in silicates is dealt with under the analysis of silicates in general (page 133).

ESTIMATION OF SODIUM IN SODIUM SALTS.

Solution.—Like the potassium salts, all the ordinary salts of sodium are dissolved by water.

Estimation as Sodium Sulphate, Na_2SO_4.—The estimations of sodium in its salts as sulphate are conducted in exactly the same manner as those given for the determination of potassium as potassium sulphate.

The presence of acid sodium sulphate must be guarded against in these estimations; it can be removed by ignition with ammonium carbonate, as in the case of the potassium salt.

The sodium in borax is estimated by warming a weighed quantity of the powdered salt with hydrofluoric acid in a platinum vessel; after a few minutes an excess of strong sulphuric acid is added in small portions at a time, then heat is applied and gradually increased until sufficient to expel the excess of sulphuric acid. The residue is weighed as sodium sulphate.

Estimation as Sodium Chloride, NaCl.—This method is applied in cases where sodium cannot be conveniently estimated as sulphate by simple treatment with sulphuric acid.

The sodium in sodium arsenate and in gold and sodium chloride may be estimated by acidifying the solution with hydrochloric acid, precipitating the arsenic or gold with hydrogen sulphide, filtering, evaporating the filtrate to dryness, igniting the residue, and weighing as sodium chloride. Sodium phosphate and pyrophosphate are estimated by precipitating their aqueous solutions with a slight excess of ferric chloride, filtering, precipitating the excess of iron salt with ammonium hydrate, again filtering, evaporating the filtrate, igniting to expel ammonium salts, and weighing the residue as sodium chloride. Sodium hypophosphite is cautiously ignited to phosphate and then treated accordingly.

To estimate the sodium in Rochelle salt, obtain the mixed chlorides of sodium and potassium, as described under the estimation of potassium in this salt on page 80, weigh them, separate the potassium in the form of potassium platinic chloride, calculate it into potassium chloride, and deduct the weight of this from the weight of the mixed chlorides; the difference is the weight of sodium chloride, from which the amount of metal may be found by calculation. The method of estimating sodium in silicates is given in the directions for the analysis of silicates on page 133.

ESTIMATION OF LITHIUM IN LITHIUM SALTS.

Solution.—Many salts of lithium are soluble in water; its common salts, which do not dissolve in water, are soluble in diluted hydrochoric acid.

Estimation as Lithium Phosphate, Li_3PO_4.—The commercial salts of lithium are liable to contain salts of other alkalies; the following method of estimation may be employed in their presence. To the solution of the lithium salt solution of sodium phosphate is added, and then sufficient sodium hydrate solution to keep the mixture alkaline. The mixture is then evaporated to dryness, and the residue treated with equal volumes of hot water and ammonium hydrate. The insoluble matter is collected upon a filter and washed with the mixture of water and ammonium hydrate until the washings give no more test for sodium. It is then dried, separated from the filter (which is burned in a spiral of platinum wire), ignited at a dull red heat, and weighed as lithium phosphate.

The filtrate and washings should be evaporated to dryness, and the residue treated with dilute ammonium hydrate; if any insoluble matter is found, it is lithium phosphate, and should be added to the first precipitate.

ESTIMATION OF AMMONIUM IN AMMONIUM SALTS.

Solution.—All the important commercial salts of ammonium are soluble in water.

Estimation as Ammonium Platinic Chloride, $(NH_4)_2PtCl_6$.—For the details of this process the operator is referred to the estimation of potassium as potassium platinic chloride, the directions given there being applicable to the salts of both bases. The precipitate of ammonium platinic chloride may be ignited, and the resulting metallic platinum weighed and taken as the basis for calculation. One atom of platinum indicates two groups of ammonium (NH_4).

Ammonium compounds are now usually estimated by volumetric analysis. The following outline of the volumetric method is given at this place because of the importance which frequently attaches to the estimation of ammonium; but, unless the operator has had experience in volumetric analysis, it may be well to postpone this experiment until he has received some instruction in the titration of acids and alkalies. To conduct this process, a flask is closely connected with the upper end of a condenser by means of a perforated cork and a bent glass tube, and a wire gauze is then brought under the flask to support it. The other end of the condenser is inserted into another flask; in this is put a known volume of normal oxalic or sulphuric acid volumetric solution. The apparatus having been arranged in this manner, the perforated cork is removed from the flask without disturbing the connection of the bent tube with the condenser. A weighed quantity of the ammonium salt is then placed into the flask on the gauze and water afterwards added to dissolve the salt, leaving room enough in the flask for the solution to boil without danger of passing into the condenser. Sufficient solution of potassium or sodium hydrate to make the liquid decidedly alkaline is next added, and the flask immediately closed by replacing the perforated cork. Heat is then applied until the solution in the flask is gently boiling, and continued until three-fourths of the solution has distilled from the flask into the receiver. A few drops of cochineal test-solution are then added to the contents of the receiving flask, and the liquid carefully titrated with normal alkali solution until the yellowish-red color is turned to violet. The number of cubic centimetres of normal acid neutralized by the ammonia gas is found by subtracting the number of cubic centimetres of normal alkali used to produce the violet color from the number of cubic centimetres of normal acid originally placed in the receiving flask, and as the value of each cubic centimetre of the normal acid solution in ammonia gas is known, the total amount of ammonia gas given off by the ammonium salt may be found by multiplication. The corresponding amount of the metal-like body ammonium is calculated from the respective molecular weights of the two substances.

ESTIMATION OF BARIUM IN BARIUM SALTS.

Solution.—Many of the salts of barium dissolve in water. Except the sulphate, all the common salts of barium which are insoluble in water dissolve in diluted hydrochloric acid. The sulphate may be changed to carbonate by fusing it with four or five times its weight of dry sodium carbonate; after thorough washing with water to remove sodium sulphate, the barium carbonate may be dissolved in diluted hydrochloric acid.

Estimation as Barium Sulphate, $BaSO_4$.—The following directions illustrate the manner in which barium is almost always estimated. Dilute sulphuric acid is added, drop by drop, to the solution of the barium salt as long as any precipitate is produced, and the mixture then boiled. The precipitate is allowed to settle, the clear, supernatant liquid poured down a glass rod into a filter, the precipitate is boiled with a fresh quantity of water, and, after pouring in the clear liquid, transferred to the filter. The precipitate is washed with hot water until the washings cease to cause a turbidity with solution of barium chloride; it is then dried, ignited, and weighed as barium sulphate.

In the absence of other non-volatile bases, barium sulphate may also be obtained from salts of barium with volatile acids by evaporating the solution of the barium salt with sulphuric acid and igniting the residue until white fumes of sulphur trioxide cease to be given off.

ESTIMATION OF STRONTIUM IN STRONTIUM SALTS.

Solution.—Strontium salts resemble those of barium, and the methods of dissolving the latter apply also to the former.

Estimation as Strontium Sulphate, $SrSO_4$.—Treat the dry salt, or evaporate its solution, with sulphuric acid and ignite as directed under barium, on page 83; or, where this procedure is inadmissible, make a moderately strong solution of the strontium compound, to this solution add sufficient dilute sulphuric acid to completely precipitate the strontium as sulphate, then add a bulk of alcohol equal to that of the mixture, stir well, and set the mixture aside for a few hours. At the end of this time filter off the precipitate, wash it with dilute alcohol, dry, ignite, and weigh. If for any reason the use of alcohol is inadmissible, the strontium sulphate must be precipitated in a more concentrated solution with dilute sulphuric acid, allowed to stand for 24 hours, collected on a filter, and washed with the least possible quantity of water.

ESTIMATION OF CALCIUM IN CALCIUM SALTS.

Solution.—With the exception of its silicates, which are dealt with under the analysis of silicates, the common salts of calcium are soluble in water or hydrochloric acid. Calcium sulphate dissolves more readily in dilute than in strong hydrochloric acid. Calcium fluoride is better decomposed by concentrated sulphuric acid; the calcium sulphate so obtained may be dissolved in dilute hydrochloric acid, or fused with sodium carbonate and the mass subsequently treated with water and hydrochloric acid, as stated for the solution of barium sulphate.

Estimation as Calcium Oxide, CaO.—Calcium is most frequently determined in this form. Mix the hot solution of the calcium compound with enough ammonium oxalate to insure complete precipitation, and then add sufficient ammonium hydrate to make the mixture alkaline to litmus. Set the mixture in a warm place and let the precipitate of calcium oxalate, CaC_2O_4, subside, decant the clear, supernatant liquid to a filter, wash the precipitate once or twice with hot water by decantation, then transfer it to the filter, and wash thoroughly with hot water. Dry and ignite the precipitate and filter. A good Bunsen burner is sufficient to effect the change of the calcium oxalate into oxide, provided the heat is continued sufficiently long. A blast-lamp will accomplish the result more quickly. The heat in either case must be continued until no further loss in weight occurs. The residue is calcium oxide. When free from contaminating non-volatile substances, calcium carbonate and calcium salts of organic acids may be estimated for calcium by direct ignition to calcium oxide with the blast-lamp.

When calcium is to be estimated in calcium phosphate, add first ammonium oxalate and then sodium acetate in excess to the hydrochloric acid solution of the salt instead of ammonium hydrate. By so doing acetic acid is liberated and prevents the precipitation of calcium phosphate along with the calcium oxalate.

Estimation as Calcium Sulphate, $CaSO_4$.—Calcium sulphide and many other calcium compounds may be estimated by converting them into calcium sulphate through evaporation with sulphuric acid and subsequent ignition.

ESTIMATION OF MAGNESIUM IN MAGNESIUM SALTS.

Solution.—The common compounds of magnesium dissolve either in water or hydrochloric acid. Magnesium silicates are treated according to the directions for the analysis of silicates.

Estimation as Magnesium Pyrophosphate, $Mg_2P_2O_7$.—This is the form in which magnesium is almost invariably weighed. A weighed quantity of the magnesium salt is dissolved, some solution of ammonium chloride added to the solution of the salt, and then ammonium hydrate until, after stirring, the mixture smells strongly of it. If the ammonium hydrate produce a precipitate it is evidence that sufficient ammonium chloride has not been added, and further additions of the latter are to be made until the precipitate is redissolved. To the clear solution ammonium or sodium phosphate is added in excess, and the mixture thoroughly stirred. The rod is not allowed to touch the sides of the beaker during the stirring, in order to prevent the precipitate from adhering to the glass. The vessel is then set aside for 12 hours at the ordinary temperature, for the precipitate of magnesium ammonium phosphate, $Mg(NH_4)PO_4$, to completely settle out. At the expiration of this time the clear, supernatant liquid is poured on a filter, and the precipitate then transferred to the same, using a little of the clear filtrate to wash the last portions on if necessary.

The precipitate is then washed with a mixture of 3 parts water and 1 part ammonia water, until a few drops of the washings, acidified with nitric acid, give no precipitate with silver nitrate.

The precipitate is then dried, transferred to a crucible, the filter burned separately, the ash added to the precipitate, and the whole ignited strongly until the weight is constant. The residue consists of magnesium pyrophosphate, $Mg_2P_2O_7$.

Should the contents of the crucible be dark in color from the carbon of the filter, moisten with nitric acid, carefully dry, and strongly reignite before weighing. When magnesium is to be estimated in the official ferric hydrate with magnesia, the precipitate of ferric hydrate, produced upon making the solution alkaline with ammonium hydrate after the addition of an excess of ammonium chloride, is removed by filtration before precipitating the magnesium with ammonium phosphate.

ESTIMATION OF MANGANESE IN MANGANESE SALTS.

Solution.—Many manganese salts are soluble in water. Those not dissolved by that menstruum are soluble in hydrochloric acid. All the oxides of manganese yield soluble manganous chloride when heated with hydrochloric acid. The higher oxides cause an evolution of chlorine when treated in the foregoing manner. For the estimation of manganese in silicates, see analysis of silicates.

Estimation as Manganous Sulphide, MnS.—This method is applicable to all manganous compounds in solution. Put the manganese compound in a flask, dissolve it, and add some ammonium chloride to the solution. If acid has been used to effect solution of the manganese compound, make the liquid neutral or faintly alkaline with ammonium hydrate. Precipitate the neutral or alkaline solution with ammonium sulphide, and if necessary fill the flask to the neck with water, then stopper it, and allow it to stand for several hours. Wash the precipitate with water containing ammonium sulphide and ammonium chloride to insure a clear filtrate, gradually decreasing the amount of the chloride till it is eventually omitted. Do the washing first by decantation, then on the filter. Dry the precipitate, transfer it to a porcelain crucible, burn the filter, add the ashes, sprinkle a little powdered sulphur on the precipitate, and ignite strongly in a current of hydrogen till the contents of the crucible become black. Weigh the product as manganous sulphide. When the filter is burned the particles of precipitate adhering to it are liable to alteration by the burning carbon, but, during the ignition, the sulphur sprinkled on the ashes reconverts any alteration products into manganous sulphide.

Estimation as Manganoso-Manganic Oxide, Mn_3O_4.—If the manganese is not already in the form of acetate, convert it into that salt by adding to the solution a sufficient quantity of sodium acetate. Now warm the solution and pass chlorine gas through it, or add bromine water, continuing the heat. The manganese is precipitated as dioxide, MnO_2. Filter off the precipitate, add more sodium acetate to the filtrate, warm, and again pass chlorine or add bromine water. If another precipitate is produced, collect it with the first one. When precipitation has been completed, wash the manganese dioxide until the washings no longer precipitate silver nitrate, then dry and ignite it, using a blast-lamp for the last purpose. Weigh the residue of ignition as manganoso-manganic oxide. The foregoing method is frequently employed in mineral analysis to separate manganese from the filtrate after precipitating iron and aluminum as basic acetates. The carbonate, oxides, and organic salts of manganese may all be converted by intense ignition into manganoso-manganic oxide and weighed in that form.

The test of standard strength given by the United States Pharmacopœia for manganese dioxide is as follows : "If 1 gm. of the finely powdered dioxide, contained in a small, long-necked flask, be mixed with 5 c.c. of water, then 4.22 gm. of ferrous sulphate, in clear crystals, added, and subsequently 5 c.c. of hydrochloric acid, the mixture digested for about fifteen minutes at a gentle heat, and finally heated to boiling, the cooled filtrate, when immediately tested with freshly prepared potassium ferricyanide test-solution, should not acquire a blue color (presence of at least 66 per cent. of pure manganese dioxide)." The explanation of this method of valuation is that the ferrous iron of the ferrous sulphate is oxidized to the ferric condition by the manganese dioxide in the presence of hydrochloric acid, the manganese of the dioxide becoming manganous chloride at the same time. If the sample contains 66 per cent. of dioxide, all of the iron of the ferrous sulphate will be changed in this manner ; if not, the remainder will be indicated by the potassium ferricyanide producing a blue color or precipitate.

ESTIMATION OF ZINC IN ZINC SALTS.

Solution.—Some of the salts of zinc are soluble in water. The metal itself and those compounds of it which are insoluble in water dissolve in hydrochloric acid.

Estimation as Zinc Oxide, ZnO.—In the absence of interfering substances, the carbonate, oxide, and organic salts of zinc may be strongly ignited and weighed as zinc oxide. The following method serves for all zinc compounds that are readily decomposed by sodium carbonate. Put the solution of the zinc compound in a porcelain dish and heat it nearly to boiling. Add to the hot liquid solution of sodium carbonate in small successive portions until the mixture is strongly alkaline to litmus, then boil for a few minutes. If ammonium salts are present the boiling must be prolonged until the vapor from the dish shows no more ammonia. The precipitate is basic zinc carbonate. Wash it first by decantation with hot water, boiling the precipitate each time with the water, then on a filter ; dry the precipitate, separate it as much as possible from the filter, burn the filter, add the ash, ignite and weigh the residue as zinc oxide. When this method is not applicable, use the next method, which can be applied to all zinc compounds.

Estimation as Zinc Sulphide, ZnS.—Zinc may be estimated in the form of sulphide by the directions given on page 86 for the determination of manganese as manganous sulphide ; or the zinc sulphide may be precipitated by hydrogen sulphide in the presence of acetic acid. In the latter method remove any free mineral acid present by adding sodium acetate, and then saturate the solution with hydrogen sulphide gas. Wash the precipitate of zinc sulphide with water saturated with hydrogen sulphide, dry it, transfer it to a crucible, burn the filter, add the ashes, and ignite with sulphur in a stream of hydrogen, as directed for manganous sulphide. The residual zinc sulphide is light in color.

Assay of Zinc Ores.—The following gravimetric method of assaying zinc ores is well suited in case of an occasional assay. When several samples are to be assayed, the volumetric process, involving the use of potassium ferrocyanide, as given in Sutton's "Volumetric Analysis," will yield the results in a shorter time. For the gravimetric process the ore is powdered, then from 0.5 to 1 gramme of the powdered substance put in a beaker and decomposed with warm hydrochloric acid with the aid of some nitric acid. When the ore is no longer acted on by the acids, the excess of the latter is evaporated, the residue treated with water, and the solution of the zinc compounds filtered from the insoluble matter into a beaker. The insoluble substances are washed with warm water to remove zinc salts, and the washings added to the filtrate in the beaker. The solution is then nearly neutralized with sodium carbonate, and the iron (with which zinc ores are almost invariably contaminated) precipitated as basic ferric acetate, as described on page 92. The washings of the basic ferric acetate are concentrated by boiling and mixed with the filtrate containing the zinc. The zinc may then be precipitated from the acid solution by means of hydrogen sulphide ; or the solution may then be made faintly alkaline with ammonium hydrate, and the zinc thrown down as sulphide by the addition of ammonium sulphide, both methods being applied according to the directions given on page 88 for the estimation of zinc as sulphide. If manganese is present, the second method of precipitating the zinc is inapplicable. When lead is present in the zinc ore, it is removed by adding sulphuric acid to the solution of the zinc in nitrohydrochloric acid, evaporating nearly to dryness, adding water, and filtering off the undissolved lead sulphate. The regular treatment for the estimation of zinc is then applied to the filtrate.

ESTIMATION OF COBALT IN COBALT SALTS.

Solution.—Water dissolves many of the salts of cobalt; all the other common compounds of this metal dissolve in hydrochloric acid.

Estimation as Metallic Cobalt, Co.—The best form in which to weigh cobalt is that of the metal itself. To obtain this, precipitate the cobalt as hydrate, $Co(OH)_2$, by adding to the hot solution of the cobalt compound a slight excess of potassium hydrate, and continue the heat to produce a brownish-black precipitate. Wash the precipitate several times by decantation with hot water, then on a filter until alkali and salts are removed. Dry the filter and contents, ignite them strongly in a crucible till the filter is consumed, then heat in a current of hydrogen to reduce the oxide of cobalt, resulting from the ignition of the hydrate, to metallic cobalt. Where the foregoing method of precipitating cobalt from solutions of its salts is inapplicable, the metal may be thrown down as sulphide, CoS, by following the directions given on page 86 for the precipitation of manganese as sulphide. The cobalt sulphide should then be dissolved in nitrohydrochloric acid, the excess of acid evaporated, the residue diluted with water, the cobalt precipitated as hydrate, as previously directed, and finally converted into metal for weighing.

The method of precipitating cobalt as potassium cobaltic nitrite, $K_6Co_2(NO_2)_{12}$, is useful in the presence of nickel salts, as the latter are precipitated by both of the methods already given for the estimation of cobalt. It is to be conducted as follows. Add to the cobalt solution a slight excess of potassium hydrate, then add sufficient acetic acid to clear the solution, and, after this, a strong solution of potassium nitrite which has been acidified with acetic acid. Now set the mixture aside for 24 hours to allow the yellow potassium cobaltic nitrite to completely settle out. If the precipitation is complete the supernatant liquid will be colorless; if so, collect the precipitate and wash it with a solution of potassium acetate containing about 10 per cent. of the salt and a small quantity of potassium nitrite. The precipitate contains variable quantities of water even when dried at 100°; for that reason it is best to dissolve the moist precipitate in hydrochloric acid and throw down the cobalt as hydrate, rather than calculate the amount of the metal from the weight of the dried potassium cobaltic nitrite.

ESTIMATION OF NICKEL IN NICKEL SALTS.

Solution.—The compounds of nickel correspond in solubility to those of cobalt. Metallic nickel dissolves slowly in hot dilute hydrochloric or sulphuric acid, but readily in nitric acid.

Estimation as Metallic Nickel, Ni.—Nickel can be precipitated from the solutions of its salts either as hydrate, $Ni(OH)_2$, or sulphide, NiS, by the methods given under the estimation of cobalt in cobalt salts, and these compounds converted into metallic nickel as described in the same place.

ESTIMATION OF IRON IN FERROUS SALTS.

Solution.—The important ferrous compounds dissolve in water or, with the exception of some of the mineral forms, in hydrochloric acid. For gravimetric analysis these native compounds are brought into solution by fusing with sodium carbonate and dissolving the mass in hydrochloric acid, but the solution so obtained contains the iron in the ferric state. Hydrochloric or dilute sulphuric acid may be used to dissolve metallic iron and yield ferrous chloride or sulphate respectively.

Estimation as Ferric Oxide, Fe_2O_3.—When iron is estimated gravimetrically it is usually precipitated in the form of ferric hydrate, the latter ignited and the residue weighed as ferric oxide. The hydrates and organic salts of iron may be converted into ferric oxide by intense ignition. On account of the tendency of ferrous compounds to change to ferric by oxidation, even by contact with air, the former, unless freshly prepared, are almost invariably contaminated with the latter; and, as both kinds of salts are precipitated by most reagents in common, it is evident that gravimetric methods do not afford a means of estimating ferrous compounds in the presence of ferric compounds. Volumetric processes for the estimation of ferrous iron in iron salts are not interfered with by the presence of ferric compounds, and are therefore employed when both kinds of salts are present.

The estimation of the iron in ferrous salts as ferric oxide requires them to be oxidized previous to precipitation. This change is brought about by adding some hydrochloric or sulphuric acid to the solution of the ferrous compound, heating the mixture to boiling, and adding nitric acid, drop by drop, until oxidation is completed, which is known to be the case when no more red-brown fumes are evolved upon the addition of more nitric acid to the hot solution, or when the solution acquires a color which is not affected by heat or more nitric acid.*

The estimation of iron in pure ferrous salts may be conducted in the following manner. Dissolve the ferrous salt, add some hydrochloric or sulphuric acid, heat the solution to boiling, and oxidize the iron with nitric acid. Then add ammonium hydrate until the solution smells strongly of it after stirring. Allow the precipitate of ferric hydrate, $Fe_2(OH)_6$, to settle, and pour the clear, supernatant liquid on a filter. Add hot water to the precipitate in the vessel, stir well, and again allow to settle. Afterwards pour the supernatant liquid on the filter, repeat the operation a few times, then transfer the precipitate to the filter and wash thoroughly with hot water until the washings cease to have an alkaline reaction and all ammonium salts have been removed. Dry the precipitate, ignite it, and weigh the residue as ferric oxide:

The preceding method is not applicable to the estimation of iron in ferrous and ferric phosphates, since these compounds are precipitated when the acid solutions containing them are made alkaline. When, therefore, phosphoric acid is present, the iron is converted into sulphide by adding ammonium hydrate and sulphide, as directed under the estimation of manganese as sulphide.

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* When nitric acid acts as an oxidizing agent it may be considered to decompose as follows:

$$2HNO_3 = H_2O + N_2O_2 + O_3.$$

The oxygen which is thus liberated then acts on the iron of ferrous compounds in the following manner:

$$6FeO + O_3 = 3Fe_2O_3.$$

The ferric oxide which is produced dissolves in the acid present to form a ferric salt. The following equations express the action of nitric acid on ferrous chloride in the presence of hydrochloric acid and the action on ferrous sulphate in the presence of sulphuric acid:

$$6FeCl_2 + 2HNO_3 + 6HCl = 3Fe_2Cl_6 + N_2O_2 + 4H_2O.$$

$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + N_2O_2 + 4H_2O.$$

Salts of iron with non-volatile organic acids (*e.g.*, tartaric and citric acids) must be treated in the same manner, since ammonium hydrate does not precipitate ferric hydrate in their presence. The ferrous sulphide, FeS, obtained in these treatments is dissolved in hydrochloric acid, the ferrous chloride oxidized by nitric acid, the resulting ferric chloride decomposed by ammonium hydrate, and the ferric hydrate ignited to oxide.

ESTIMATION OF IRON IN FERRIC SALTS.

Solution.—Water dissolves many ferric compounds; those insoluble in water dissolve in hydrochloric acid. Native ferric compounds frequently require fusion with sodium carbonate or potassium disulphate before solution in hydrochloric acid can be effected. Ferric oxide which has been very strongly heated usually requires a similar treatment.

Estimation as Ferric Oxide, Fe_2O_3.—Dissolve the ferric salt, and, omitting the addition of an acid and the treatment with nitric acid, proceed with the estimation exactly as stated for ferrous salts. When iron is to be estimated in the ferric hydrate with magnesia of the Pharmacopœia, the addition of ammonium hydrate must be preceded by that of an excess of ammonium chloride to prevent the precipitation of magnesium hydrate. Ferric phosphate, hypophosphite, and organic salts with non-volatile acids are to be estimated by the directions given for ferrous phosphate.

Another useful method of precipitating iron, and one which is often employed in the analysis of minerals containing this metal, depends upon the formation of insoluble basic ferric acetate ($Fe_2(C_2H_3O_2)_4(OH)_2$) when a solution containing ferric acetate is boiled. This process is conducted by adding to the solution of the ferric salt sodium carbonate until the liquid is no longer acid but still remains clear; some acetic acid is now added, afterwards about ten times as much crystallized sodium acetate as there is iron present, and the solution then boiled for a few minutes. The operation has been successful if the precipitate settles rapidly and leaves a clear, supernatant liquid when the flame is withdrawn. The quantity of acetic acid present should never exceed 4 per cent., by volume, of the ordinary concentrated acid; when iron alone is present, little or none is needed. After being washed, the precipitate may be ignited to ferric oxide, or it may be dissolved in hydrochloric acid, the iron precipitated as hydrate and then converted into oxide by ignition.

For the complete analysis of iron ores consult Fresenius' "Quantitative Analysis."

ESTIMATION OF CERIUM IN CERIUM SALTS.

Solution.—Cerous chloride, sulphate, and nitrate are soluble in water; cerous oxalate, carbonate, and phosphate dissolve in hydrochloric acid.

Estimation as Ceric Oxide, CeO_2.—Cerium oxalate may be converted into ceric oxide by direct ignition, and weighed in that form, provided, of course, that the product of ignition is free from other non-volatile substances.

The salts of cerium in general may be estimated by precipitating the boiling solution of the substance with potassium hydrate, washing the precipitate of cerous hydrate, $Ce_2(OH)_6$, drying it, igniting to redness, and weighing the resulting ceric oxide.

ESTIMATION OF ALUMINUM IN ALUMINUM SALTS.

Solution.—The solution of the compounds of aluminum may be effected by the solvent required for the corresponding ferric compound. The methods of solution which are given in the analysis of silicates may be used for decomposing the aluminum silicates and bringing the base into solution. The metal may be dissolved in hydrochloric acid.

Estimation as Aluminum Oxide, Al_2O_3.—When alone, the aluminum salts of organic acids, as also the nitrate and hydrate, may be changed to aluminum oxide by strong ignition. In most other cases the solution of the aluminum compound is mixed with some ammonium chloride and a slight excess of ammonium hydrate added. The mixture is then boiled, to expel ammonia, until it shows but a very faint alkaline reaction. When these conditions are obtained, the precipitate of aluminum hydrate, $Al_2(OH)_6$, is permitted to settle, the clear liquid above it decanted on a filter, the precipitate washed repeatedly by decantation with boiling water, finally transferred to a filter, and the washing completed. The precipitate is then dried and ignited. The residue is aluminum oxide.

When phosphate of aluminum is to be analyzed, proceed as in the case of the phosphates of iron (page 91).

ESTIMATION OF CHROMIUM IN CHROMIUM SALTS AND CHROMATES.

Solution.—The chromium salts closely resemble those of aluminum and ferric iron in points of solubility. Chromic oxide, which has been rendered insoluble in acids by strong ignition, may be dissolved to chromic chloride by fusing it with several times its weight of potassium hydrate and then treating the mass with hot hydrochloric acid. The chromates and dichromates of the alkali metals dissolve in water; the other chromates dissolve in hydrochloric or nitric acid.

Estimation as Chromic Oxide, Cr_2O_3.—This method is suitable for the analysis of the salts of chromium. Heat the solution of the chromium compound nearly to boiling and add ammonium hydrate in slight excess. Continue the heat near boiling until the supernatant liquid is entirely free from color, allow the precipitate of chromic hydrate, $Cr_2(OH)_6$, to subside, wash it several times with hot water by decantation, afterwards complete the washing on a filter, dry, and ignite the precipitate. The product of ignition is chromic oxide.

Chromates may be reduced to chromic chloride by adding hydrochloric acid to their solutions, warming, and saturating the solution with sulphur dioxide, or adding alcohol; in the absence of other bases precipitable by ammonium hydrates, the chromium may then be precipitated as hydrate, and weighed as oxide, according to the method already outlined. Lead, and the heavy metals in general, are precipitated from their acid solutions with hydrogen sulphide, before throwing down the chromium hydrate, by the addition of ammonium hydrate.

Estimation as Lead Chromate, $PbCrO_4$.—When the chromium of an alkali chromate is to be estimated proceed as follows. Mix the solution of the chromate with an excess of sodium acetate, acidify the mixture with acetic acid. and add neutral lead acetate until precipitation is completed. Collect the precipitate of lead chromate on a weighed filter, wash it with water, dry at 100°, and weigh as anhydrous lead chromate.

If it is desired to oxidize the chromium of a chromic compound to the acid condition for estimation as lead chromate, make the solution nearly neutral, if necessary, with sodium carbonate, add sodium acetate in excess, apply heat to the solution and pass chlorine gas through it, or add chlorine water, occasionally adding sodium carbonate to keep the solution from becoming strongly acid with hydrochloric acid; finally expel the excess of chlorine by heat before adding more sodium acetate and precipitating the chromate with lead acetate.

ESTIMATION OF ARSENIC IN ARSENOUS COMPOUNDS.

Solution.—Many of the important arsenous and arsenic compounds are soluble in water, the others dissolve either in hydrochloric or nitrohydrochloric acid; the last solvent dissolves metallic arsenic also. Arsenous sulphide may be brought into solution by treating it with nitrohydrochloric acid, or by dissolving it in a concentrated solution of potassium hydrate and saturating the solution with chlorine. Fusion with sodium carbonate and potassium nitrate is often a useful step in the solution of metallic arsenates and arsenides. When oxidizing agents have been used in dissolving the substance, the solution will contain more or less arsenic in its higher state of oxidation. If a hydrochloric acid solution of arsenic is to be concentrated, it should be made alkaline previous to evaporation, in order to prevent loss of arsenic by volatilization.

Estimation as Arsenous Sulphide, As_2S_3.—As hydrogen sulphide precipitates both arsenous and arsenic compounds, the method about to be given can be used to estimate the arsenic of either class of compounds, or the total arsenic of a mixture of these compounds, but obviously not for the estimation of the arsenic of one class in the presence of the other.

To obtain the arsenous sulphide for weighing, make the solution of the arsenous compound strongly acid with hydrochloric acid and precipitate it with hydrogen sulphide gas. After the solution has been thoroughly saturated with this reagent, warm the mixture, and expel the excess of hydrogen sulphide by conducting a current of carbon dioxide into the solution for an hour. Collect the precipitate of arsenous sulphide on a tared or balanced filter, wash it thoroughly, and dry at 100° till the weight is constant. The precipitate should completely volatilize on the application of a strong heat; a weighed portion of the dried precipitate should always be treated in this manner, and if any residue remains, a correction should be made by deducting a proportional amount from the weight of the whole precipitate.

The dried arsenous sulphide should also be tested for sulphur by digesting it with purified carbon disulphide; if the latter upon separation and evaporation leaves a residue of sulphur, the extraction must be carried to completion, the arsenous sulphide again dried and weighed, and its weight corrected for sulphur also.

ESTIMATION OF ARSENIC IN ARSENIC COMPOUNDS.

Solution.—See solution of arsenous compounds.

Estimation as Arsenous Sulphide, As_2S_3.—Follow the directions given for the estimation of arsenous compounds as arsenous sulphide, but heat the solution, during the passing of the hydrogen sulphide gas, to 70°. The precipitate in the case of arsenic compounds is a mixture of arsenous sulphide and sulphur. To purify the sulphide for weighing, collect the precipitate on a filter, treat it while still moist with ammonium hydrate, wash the sulphur which remains on the filter with water, mix the washings with the ammoniacal solution, and precipitate the mixture with an excess of hydrochloric acid. Filter off the arsenous sulphide, wash it thoroughly, dry it, treat with carbon disulphide as mentioned under arsenous compounds, then dry at 100° till the weight is constant.

Estimation as Magnesium Ammonium Arsenate, $MgNH_4AsO_4.H_2O$.—For this determination the arsenic must be in the form of arsenic acid or a salt of it. Arsenous compounds may be oxidized to arsenic compounds by warming the solution with hydrochloric acid, and adding potassium chlorate little by little until the liquid has a strong odor of chlorous acid ; the excess of this gas is then expelled by continuing the application of the heat. The solution of the arsenic compound is rendered alkaline with ammonium hydrate, and magnesia mixture then added until no more precipitation takes place. The mixture is let stand twenty-four hours, and the precipitate then collected on a balanced filter, some of the first filtrate being used to wash the last portions of the precipitate from the beaker to the filter. The precipitate is washed with a mixture of water and ammonium hydrate, as directed in the estimation of magnesium, and finally, when free from chlorides, dried to a constant weight at from 102° to 103°. This method may be used to separate arsenic acid from arsenous acid.

ESTIMATION OF ANTIMONY IN ANTIMONY COMPOUNDS.

Solution.—Tartar emetic is the most important antimony compound that gives a clear solution with water. Hydrochloric acid dissolves the remaining compounds with more or less readiness. Metallic antimony may be dissolved in nitrohydrochloric acid. Solutions of antimonous chloride must be mixed with tartaric acid previous to dilution with water, otherwise insoluble basic compounds will be formed. Boiling hydrochloric acid solutions of antimonous chloride lose material through volatilization ; hence a solution of this character, to be concentrated, must be previously rendered alkaline.

Estimation as Antimonous Sulphide, Sb_2S_3.—The following method applies to both antimonous and antimonic compounds. If the antimony solution has not been prepared by means of hydrochloric acid, it should be acidified with the same, then mixed with tartaric acid and diluted with water, care being taken to preserve it clear. Now precipitate the liquid by passing hydrogen sulphide through it until the mixture is thoroughly saturated ; then warm the mixture, and expel the excess of hydrogen sulphide by passing carbon dioxide into the mixture. Collect the precipitate without delay on a balanced filter, wash it with water, and dry at 100° till the weight is constant. The weighed precipitate may not be pure, however, since it is impossible, or nearly so, to remove the last traces of water from the antimonous sulphide by drying at 100° ; and besides, when antimonic compounds are present the antimonous sulphide will be mixed with sulphur. To test the precipitate for sulphur, treat a portion of the dried material with concentrated hydrochloric acid ; if it dissolves without turbidity, sulphur is absent. The antimonous sulphide may be freed from both water and sulphur by placing a known weight of it in a porcelain boat, introducing this into a wide glass tube through which a current of carbon dioxide is passing, and carefully heating the tube along the whole length of the boat until the orange-colored antimonous sulphide becomes black. When sulphur is present the heat must be more intense and continued for a longer time. After this treatment the residue in the boat is pure anhydrous antimonous sulphide.

Estimation as Antimony Tetroxide, Sb_2O_4. — Metallic antimony, when unmixed with tin or other substances insoluble in nitric acid, may be converted into antimonous oxide, Sb_2O_3, by evaporating on the water-bath with dilute nitric acid until all metallic particles have disappeared. After washing, the antimonous oxide is changed to antimony tetroxide by strong ignition. The antimony of alloys is frequently weighed in this form.

ESTIMATION OF TIN IN STANNOUS SALTS.

Solution.—The chlorides of tin are soluble in water, but show a disposition to form insoluble hydroxychlorides with it, unless a small quantity of hydrochloric acid is added. The stannates of the alkali metals are also soluble in water. Hydrochloric or nitrohydrochloric acid will dissolve the remaining important compounds of tin. Metallic tin is soluble in hydrochloric acid or aqua regia. Stannic oxide which has been rendered insoluble in hydrochloric acid by intense ignition dissolves in that liquid after being fused with caustic alkali.

Estimation as Stannic Oxide, SnO_2.—The estimation of the tin in stannous salts requires the latter to be changed to the stannic condition by the addition of an excess of chlorine, either as gas or dissolved in water, to the solution of the stannous salt. When the solution no longer contains anything but stannic salts it is ready for the precipitation of the tin. Any large excess of hydrochloric acid is to be removed by adding ammonium hydrate until the liquid is nearly neutral. The slightly acid fluid is now to be mixed with a strong solution of ammonium nitrate, or sodium sulphate, and heated for some time, to precipitate the tin as stannic acid, H_2SnO_3.* The precipitate should be washed several times by decantation, finally collected on a filter, washed thoroughly, dried, and ignited with a blast-lamp. The product of ignition is stannic oxide.

To obtain stannic oxide from metallic tin, as in the analysis of alloys, treat the metal in small pieces with a mixture of equal volumes of nitric acid and water, and cautiously apply heat until all metallic particles have disappeared and the residue of metastannic acid, $H_{10}Sn_5O_{15}$, is of a uniformly white color. Now evaporate the mixture nearly to dryness on a water-bath, add water, filter off the precipitate, wash it free from acid, dry, ignite, and weigh as stannic oxide.

ESTIMATION OF TIN IN STANNIC SALTS.

Solution.—The solution of tin and its compounds is dealt with under the estimation of stannous salts.

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* The reactions are expressed by the following equations:

$$SnCl_4 + 4NH_4NO_3 + 3H_2O = H_2SnO_3 + 4NH_4Cl + 4HNO_3.$$

$$SnCl_4 + 4Na_2SO_4 + 3H_2O = H_2SnO_3 + 4NaCl + 4NaHSO_4.$$

Estimation as Stannic Oxide, SnO_2.—Proceed with the solution of the stannic compound in the manner described for the estimation of stannous salts as stannic oxide.

ESTIMATION OF GOLD IN GOLD SALTS.

Solution.—The haloid salts of gold are soluble in water. Metallic gold and those of its salts insoluble in water dissolve in aqua regia, or in strong chlorine water, to form auric chloride.

Estimation as Metallic Gold, Au.—Metallic gold may be obtained from its compounds, for weighing, by strong ignition, when no fixed acid or other substance is present. But when the gold salt is mixed with non-volatile or difficultly volatile substances, as in the case of the gold and sodium chloride of the United States Pharmacopœia, the metal must be precipitated from the interfering substances before it can be weighed. The following directions of the Pharmacopœia for the valuation of the salt referred to will illustrate the methods usually adopted for the separation of gold under such circumstances: "If 0.5 gm. of gold and sodium chloride be dissolved in 50 c.c. of water, in a porcelain capsule, the solution acidulated with 5 c.c. of diluted sulphuric acid, and, after the addition of 1 gm. of pure oxalic acid, heated for about two hours on a water-bath, a precipitate of metallic gold will be obtained, which, when washed, dried, and ignited, should weigh not less than 0.15 gm. (corresponding to at least 30 per cent. of metallic gold)."

Ferrous sulphate is sometimes used instead of oxalic acid to precipitate the gold.

The estimation of gold in alloys is conveniently effected by cupellation. For this purpose, the alloy is enveloped in three or four times its weight of lead-foil, the package placed in a cupel of bone ash, and the latter with its contents put into a reverberatory furnace and heated. The lead and other base metals are oxidized by the intense heat and absorbed in the cupel, while the gold (and silver and platinum if present in the alloy) remains as metal in a molten globule. When the surface of the so-called button ceases to be covered with iridescent films, and exhibits a brilliant appearance, the cupel is removed from the furnace, allowed to cool, the button removed, flattened if necessary, and weighed. If silver is present, and the quantity of it is small, the button is flattened into a thin sheet and treated with cold dilute nitrohydrochloric acid, which dissolves the gold and platinum to chlorides and leaves the silver as insoluble silver chloride; larger quantities of silver are removed by boiling the thinly flattened alloy with nitric acid of 1.3 sp. gr. In the latter case the undissolved gold is washed, ignited, and weighed. Platinum may be separated from the solution of the gold chloride, as ammonium platinic chloride, by the instructions given under the estimation of platinum, and the gold precipitated from the filtrate by means of oxalic acid or ferrous sulphate.

For the assay of gold ores the reader is referred to Brown's "Manual of Assaying," or some other special treatise on the subject.

ESTIMATION OF PLATINUM IN PLATINUM SALTS.

Solution.—Platinic chloride is soluble in water; metallic platinum and the compounds of it which are insoluble in water may be dissolved to platinic chloride by treatment with nitrohydrochloric acid.

Estimation as Metallic Platinum, Pt.—In the absence of other non-volatile substances metallic platinum may be obtained from its compounds by simple ignition. Or it may be precipitated as potassium or ammonium platinic chloride and, by subsequent ignition of these compounds, obtained as metal. The process is conducted as follows. Have the platinum in the form of platinic chloride, make sure no considerable amount of free acid is present, and that the solution is in a concentrated condition. Add to the solution ammonium chloride, then mix in a large quantity of alcohol. Let the mixture stand in a closely covered vessel for several hours. If the fluid is free from color all of the platinum is precipitated, in which case collect the ammonium platinic chloride, $(NH_4)_2PtCl_6$, on a filter, wash it with 80 per cent. (by volume) alcohol,* dry, and ignite it. The residue is metallic platinum.

For the estimation of platinum in alloys see the directions for the cupellation of alloys of gold on page 99.

ESTIMATION OF MERCURY IN MERCURIC SALTS.

Solution.—Mercuric chloride and nitrate are soluble in water. Mercuric sulphide is soluble in nitrohydrochloric acid, which is also a good solvent for metallic mercury. The mercuric oxides and other remaining mercuric compounds are dissolved by hydrochloric and nitric acids. Mercurous compounds are converted into mercuric compounds when subjected to the action of oxidizing agents. When metallic mercury is dissolved in nitric acid, the latter must be diluted and heat avoided, or oxidation to mercuric nitrate will take place. In all cases as little nitric acid as possible should be used.

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* Rules for making an alcohol of any required lower percentage from an alcohol of any given higher percentage will be found on page 317.

Estimation as Mercuric Sulphide, HgS.—If the mercuric compound is in plain aqueous solution, acidify the latter with hydrochloric acid; but if acid was used to dissolve its substance, dilute the solution with water. Now precipitate the mercury with hydrogen sulphide gas, and, after allowing the mercuric sulphide to settle, collect it on a balanced filter, wash it with cold water, and dry it at 100° till the weight is constant.

If, from the presence of free chlorine, nitric acid, or any other cause, the precipitate should contain free sulphur, it is washed on the filter with two successive portions of strong alcohol to remove the water, and then with carbon disulphide to remove the impurity. Finally, it is dried at 100°.

Estimation as Mercurous Chloride, Hg_2Cl_2.—Acidify the solution of the mercuric compound with hydrochloric acid, add an excess of phosphorous acid, and allow the mixture to stand for several hours, or heat it on a boiling water-bath for one hour, that the precipitation of the mercurous chloride shall be complete. Then collect the precipitate on a balanced filter, wash it, and dry it to a constant weight at 100°. The filtrate should be boiled to prove that the precipitation is complete.

The reduction of the mercuric compound is brought about by the phosphorous acid, which is oxidized to phosphoric acid. Water which has been in contact with phosphorus for some time may be used to supply the phosphorous acid.

ESTIMATION OF MERCURY IN MERCUROUS SALTS.

Solution.—Mercurous nitrate is soluble in water, but the presence of much of the solvent decomposes the salt into an insoluble basic form; if a little cold dilute nitric acid is added to the water, the formation of the basic salt is prevented, and a clear solution is obtained. As a rule, mercurous compounds insoluble in water dissolve in nitric acid; but the latter must be applied in a diluted condition and heat avoided, or oxidation to the mercuric state will follow. Mercurous chloride and iodide may be dissolved in nitrohydrochloric acid, which converts them into mercuric chloride.

Estimation as Mercurous Chloride, Hg_2Cl_2.—If much nitric acid is used to dissolve the substance, the solution of the mercurous compound should be nearly neutralized with sodium carbonate before precipitation is undertaken. Dilute the solution of the mercurous compound well with water, and add to it enough solution of sodium chloride to effect complete precipitation. After the precipitate has thoroughly settled, collect it on a balanced filter, wash it with water, dry at 100°, and weigh.

Estimation as Mercuric Sulphide, HgS.—This method may be employed in the case of those mercurous salts which must be oxidized to the mercuric condition in order to bring them into solution.

The mercuric solution so obtained is treated according to the directions given on page 101 for the estimation of mercury in mercuric salts as sulphide.

ESTIMATION OF BISMUTH IN BISMUTH SALTS.

Solution.—Most of the bismuth salts are insoluble in water, or form compounds insoluble in that liquid when treated with it. Hydrochloric acid or nitric acid dissolves the compounds of bismuth which are insoluble in water, but if the solutions are diluted with excessive volumes of water, insoluble basic chloride or nitrate will be thrown down. Metallic bismuth dissolves in nitric or nitrohydrochloric acid.

Estimation as Bismuth Trisulphide, Bi_2S_3.—All the salts of bismuth may be estimated as trisulphide. Add some acetic acid to the solution of the bismuth compound, and dilute to a suitable bulk with water. The addition of acetic acid prevents the precipitation of basic bismuth salts by the water. Pass hydrogen sulphide gas into the solution until it is thoroughly saturated; allow the precipitate to settle, pour off the clear supernatant liquid through a balanced filter, make sure that precipitation is complete by diluting the filtrate with water and again applying hydrogen sulphide, collect the bismuth sulphide on the filter, and wash it with hydrogen sulphide water. Dry at 100°, without delay, and weigh. If the conditions of precipitation are such as to cause a separation of sulphur, the bismuth sulphide must be treated with carbon disulphide to remove this impurity. Directions for this treatment will be found under the estimation of mercury as mercuric sulphide on page 101.

Estimation as Bismuth Trioxide, Bi_2O_3.—When free from non-volatile impurities, the basic carbonate and nitrate of bismuth may be converted into trioxide, for weighing, by simple ignition. This method is also applicable to the bismuth salts of organic acids. In all cases the heat must finally be raised till the bismuth trioxide fuses.

Estimation as Metallic Bismuth, Bi.—Bismuth sulphide and oxide may be reduced to metallic bismuth by fusion with 5 or 6 times their weight of potassium cyanide. Mix the materials in a weighed porcelain crucible, using the proportions given and stirring them well together; then apply heat until fusion takes place, and maintain this condition for some minutes. The bismuth separates to the bottom of the crucible in the form of metallic globules. Allow the crucible and its contents to cool, treat the mass with water, collect the metallic particles on a weighed filter, wash them with water, follow this with diluted alcohol, and this again with plain alcohol. Put the filter and contents into the original crucible, and dry the whole to a constant weight at 100°. This procedure is adopted to guard against inaccuracies that might arise from particles of porcelain being detached from the crucible and weighed as bismuth. From the total weight deduct the combined weight of the filter and crucible; the difference is the weight of metallic bismuth. When bismuth sulphide is to be reduced, a greater heat and a longer duration of it will be needed than for the oxide. If, in the reduction of the sulphide, any black powder is found upon treating the fused mass with water, it is evidence of incomplete reduction, and the process must be repeated.

ESTIMATION OF COPPER IN COPPER SALTS.

Solution.—Water dissolves many of the most important compounds of copper. Copper salts insoluble in water dissolve in nitric or hydrochloric acid. Metallic copper is most conveniently dissolved in nitric acid.

Estimation as Cupric Oxide, CuO.—Copper salts of organic acids and copper carbonate, nitrate, and sulphate may be converted into cupric oxide, for weighing, by the application of intense heat; provided, of course, that no other non-volatile substance is present.

The cupric salts soluble in water may be estimated as follows:

A weighed quantity of the salt is dissolved in water in a porcelain dish, and boiled with a slight excess of potassium hydrate solution until the cupric hydrate, $Cu(OH)_2$, which is first formed, is converted into black cupric oxide. The precipitate is washed two or three times by boiling with fresh portions of water, decanting each time; it is then transferred to the filter and washed with hot water until the washings cease to change red litmus paper. The precipitate is dried, and when possible separated from the filter; the latter is burned on the crucible lid, and the residue, after burning, is moistened with a drop or two of nitric acid, and again heated to reconvert into oxide any metallic copper that may have been formed by the reducing action of the burning paper. This residue is then transferred to the crucible with the precipitate, and the whole ignited and weighed. The product is cupric oxide.

The presence of non-volatile organic substances, such as tartaric acid and sugar, renders the precipitation of copper by fixed alkalies incomplete or prevents it altogether. Therefore, to apply the foregoing method in such cases, the organic matter must be destroyed by igniting the substance in a porcelain crucible; the residue may then be dissolved in dilute nitric acid and the process conducted as described.

Estimation as Cuprous Sulphide, Cu_2S.—This method may be applied to all copper compounds in solution, and is not interfered with by the presence of organic matter.

Precipitate the sufficiently dilute and acidified solution of the copper compound with hydrogen sulphide. If nitric acid is absent, heat the solution nearly to boiling during the precipitation, in order to make the precipitate of cupric sulphide, CuS, denser, and, on that account, easier to wash. Collect the precipitate on a filter, wash it with hydrogen sulphide water, and dry it quickly. Put the precipitate in a porcelain crucible, burn the filter, add the ash, and, after strewing some powdered sulphur on the contents of the crucible, strongly ignite the whole in a current of hydrogen. Weigh the residue as cuprous sulphide.

Estimation as Metallic Copper, Cu.—This process is conducted in a porcelain dish. If the solution of the copper compound contains nitric acid, remove it by evaporation with hydrochloric acid. Put a piece of zinc into the solution, and, if the latter does not contain sufficient hydrochloric acid to cause an evolution of hydrogen, add some of this acid. Place a watch-glass over the dish. The copper separates in red masses. Prolong the evolution of hydrogen, and after the expiration of a few hours test a few drops of the liquid with a drop of potassium ferrocyanide test-solution; if no brown precipitate forms, the precipitation of the copper is complete. When this is the case, and no hard particles of zinc can be felt with the glass rod, collect the precipitated copper on a balanced filter, wash it with boiling water to remove acid, then with alcohol to displace the water, dry the copper at 100° and weigh it. Metallic cadmium may be used instead of zinc. Either metal must dissolve in hydrochloric acid without residue.

Assay of Copper Ores.—When arsenic, antimony, bismuth, cadmium, and tin are absent, an occasional assay of a copper ore may be conveniently made as follows. From 1 to 5 grammes of the powdered ore, according to the probable amount of copper present (the smaller amount in the case of rich ores, the larger amount in the case of poor ones), are put into a beaker holding from 200 to 250 c.c. A mixture of one volume of strong sulphuric acid and three or four volumes of strong nitric acid is made in another beaker by pouring the first-named acid, during constant stirring, into the last-named acid. The powdered ore in the beaker is then treated with from 20 to 25 c.c. of this acid mixture for each gramme of ore present, the mixture being poured upon the ore. A watch-glass is then put over the beaker, and the mixture heated on a sand-bath to 100° until the action of the acids ceases. The cover is then removed from the beaker, and the heat continued until the odor of nitric acid is no longer perceptible. The treatment with acids converts the copper into sulphate, but the latter is mixed with impurities from the ore and must be separated from them. For this purpose, the beaker and contents are allowed to cool after complete expulsion of the nitric acid; the beaker is then half filled with water and the mixture digested for fifteen minutes or so on a sand-bath to dissolve the copper sulphate. When the solution of the copper salts is apparently effected, the mixture is filtered, and the insoluble residue washed with hot water. The washings and filtrate are mixed, acidified with hydrochloric acid, heated to boiling, and precipitated with hydrogen sulphide. When the precipitation is completed, the precipitate of cupric sulphide is collected, washed, dried, and ignited in hydrogen, as directed under the estimation of copper as cuprous sulphide on page 104. When antimony, arsenic, bismuth, cadmium, and tin are present, the copper ore is treated with nitrohydrochloric acid instead of the mixture of sulphuric and nitric acids. The nitrohydrochloric acid is made by mixing one volume of concentrated nitric acid with four volumes of concentrated hydrochloric acid. After decomposition in the foregoing manner, the solution of the copper compounds is mixed with enough sulphuric acid to change all nitrates and chlorides present into sulphates, but a large excess is avoided. The mixture is then evaporated to expel the nitric and hydrochloric acids from their salts and to obtain the copper in the form of sulphate. The copper sulphate is removed from the residue by treatment with warm water, filtration, and washing. The filtrate is mixed with sulphurous acid in such quantity as to impart an odor that will be permanent after the solution has stood in a warm place for four or five hours. When sufficient of the reagent has been added to produce this effect, and the solution has stood for the specified time, the copper is precipitated by the addition of a very small excess of potassium sulphocyanate. The precipitate of cuprous sulphocyanate is allowed to settle, collected on a filter, washed, dried, mixed with sulphur, and ignited in hydrogen, as in the case of cupric sulphide. The product of ignition is cuprous sulphide.

ESTIMATION OF CADMIUM IN CADMIUM SALTS.

Solution.—Many of the cadmium salts are soluble in water; the metal and its remaining compounds dissolve in hydrochloric or nitric acid.

Estimation as Cadmium Sulphide, CdS.—This form may be used to estimate all of the cadmium compounds. Make a dilute solution of the cadmium compound, and have it just distinctly acid with hydrochloric acid. Pass hydrogen sulphide gas into this solution till precipitation is complete. Collect the precipitate on a balanced filter, wash it with hydrogen sulphide water, and dry it at $100°$ till the weight is constant.

Estimation as Cadmium Oxide, CdO.—The nitrate, carbonate, and salts of cadmium with organic acids may be converted into cadmium oxide by ignition and weighed, when other non-volatile substances are absent. The salts of cadmium which are soluble in water may readily be weighed as oxide by precipitating the solution with sodium carbonate and igniting the precipitate, as directed in the estimation of zinc as oxide on page 87.

ESTIMATION OF SILVER IN SILVER SALTS.

Solution.—A few of the compounds of silver are soluble in water; silver nitrate is the most important of these. With the exception of silver chloride, bromide, and iodide, the salts of silver and the metal itself dissolve in more or less concentrated nitric acid; in the case of the metal the nitric acid solution should finally be boiled to expel nitrous acid. Silver chloride, bromide, and iodide may be put in a porcelain crucible and reduced to metallic silver by igniting to redness in a current of hydrogen ; silver cyanide may readily be reduced to metal by simple ignition. If necessary, the metal is dissolved in nitric acid and precipitated as silver chloride.

Estimation as Silver Chloride, AgCl.—This method is applicable to all silver salts soluble in water or nitric acid. Make a dilute solution of the silver compound. If it does not already contain nitric acid, add some of the same, and heat to about 70°. Then completely precipitate the solution with dilute hydrochloric acid, added in small portions during constant stirring, and continue the heat until the precipitate settles and a clear, supernatant liquid is obtained. Collect the silver chloride on a balanced filter, wash it with hot water till free from acid, and dry it to a constant weight at 130°. Or the silver chloride may be collected on an ordinary filter, the precipitate and filter washed and dried, the precipitate transferred to a porcelain crucible, and the filter burned on the crucible lid. If an appreciable amount of the precipitate adheres to the filter, it is best to moisten the burned residue with a drop or two of nitrohydrochloric acid, to reconvert any metallic silver which may have been formed into chloride. The small residue on the lid is then transferred to the crucible, the lid put on the latter, and the whole heated in an air-bath to 130° until the weight is constant. The weight, after deducting that of crucible, lid, and ash, is the amount of silver chloride.

Instead of simply drying the silver chloride in the crucible, it may be cautiously heated till it begins to fuse at the edge, then cooled and weighed.

All of the foregoing operations should be conducted as rapidly as possible, because silver chloride is decomposed by the light.

Estimation as Metallic Silver, Ag.—Silver salts of organic acids and silver compounds in general, except those with non-volatile inorganic acids, may be converted into metallic silver by ignition, some in hydrogen. The substance should be ignited in a porcelain crucible and the heat gradually increased to redness. When the haloid compounds of silver are to be reduced in this manner a current of hydrogen should be passed into the crucible during the ignition.

The silver contained in alloys may be estimated by the cupellation process described in connection with the estimation of gold in alloys. Should the button of metallic silver contain gold, treat it with nitric acid as there directed, weigh the undissolved gold, and deduct its amount from the weight of the button to find the quantity of silver present. For the assay of silver ores the reader is referred to Brown's "Manual of Assaying" or some other special treatise on the subject.

ESTIMATION OF LEAD IN LEAD SALTS.

Solution.—The acetate and nitrate are the principal salts of lead which dissolve in water. Metallic lead, litharge, and most of the compounds of lead insoluble in water are soluble in dilute nitric acid. Lead dioxide and red lead may be dissolved by heating them with dilute nitric acid and gradually adding alcohol till solution is effected. Lead chloride, bromide, and iodide may be decomposed by boiling with sodium carbonate, and the resulting lead carbonate converted into oxide by ignition and weighed, or dissolved in nitric or acetic acid and precipitated as sulphate or sulphide. Lead sulphate dissolves in solution of ammonium acetate or tartrate; from this liquid the lead may be precipitated as sulphide by means of hydrogen sulphide.

Estimation as Lead Monoxide, PbO.—Lead monoxide is a convenient form in which to weigh the lead of lead compounds easily decomposable into this substance by the direct application of heat. Lead monoxide, acetate, carbonate, and nitrate are all conveniently weighed as such, if unmixed with non-volatile substances. The ignition is conducted in a porcelain crucible, which is heated gently at first but finally brought to redness. The organic salts of lead are first thoroughly carbonized by a gentle heat, the crucible allowed to cool, its contents covered with a layer of fused ammonium nitrate, the whole, thereafter, gradually heated to redness, and this temperature maintained till no more fumes are evolved. When the weight of the product of ignition is constant, it is calculated as lead monoxide. The addition of ammonium nitrate prevents the separation of metallic lead and assists in the combustion of the carbon.

Estimation as Lead Sulphate, $PbSO_4$.—Add dilute sulphuric acid to the solution of the lead compound until it no longer causes a precipitate, then add to the mixture twice its volume of alcohol, and set the vessel aside for the precipitate to settle. Collect the precipitate, wash it with alcohol, dry it, separate it from the filter, ignite the precipitate and filter in a porcelain crucible, and weigh the residue as lead sulphate. The addition of alcohol may be omitted if a somewhat larger quantity of dilute sulphuric acid is used to throw down the lead, but the precipitation is not likely to be complete unless alcohol is employed. Nitric acid tends to render the precipitation of the lead sulphate incomplete. If, therefore, it was used in dissolving the lead compound, it should be removed by adding sulphuric acid to the solution and evaporating on the water-bath ; the alcohol may then be added, unless its use is precluded, and the estimation carried out as already outlined. If the ignited lead sulphate is not pure white in color, it should be moistened with sulphuric acid and again ignited until white fumes are no longer given off.

Estimation as Lead Sulphide, PbS.—All lead salts may be estimated by this method. The solution of the lead salt should not contain a large amount of free acid. If acid (usually nitric) was required to dissolve the substance, and much of it was used for the purpose, the solution should be nearly neutralized with sodium carbonate.

To precipitate the lead as sulphide, pass hydrogen sulphide gas into the cold solution until the latter smells strongly of the reagent. Filter off the precipitate, wash it with cold water, and dry it. Separate the precipitate from the filter, transfer it to a porcelain crucible, burn the filter, allow the ash to fall on the precipitate in the crucible, cover the contents of the crucible with powdered sulphur, and ignite in a current of hydrogen to dull redness. Make sure the weight of the lead sulphide is constant by reigniting and weighing again. Neutral and alkaline solutions of lead compounds may be precipitated by means of ammonium sulphide, and the lead sulphide prepared for weighing as just described.

Assay of Lead Ores.—The following method of assaying lead ores is applicable to galenas and carbonates, unless arsenic or antimony is present, when the results are a trifle low. If the preliminary qualitative analysis reveals the presence of these substances, the alternative method which follows should be employed. From 2 to 5 grammes of the finely powdered ore are placed in a beaker of about 200 c.c. capacity. In another beaker one volume of concentrated sulphuric acid is mixed with three or four volumes of concentrated nitric acid by gradually pouring the former into the latter during constant stirring. Some of this acid mixture is poured upon the powdered ore in the first beaker; from 20 to 25 c.c. of the mixture is used for each gramme of ore taken for analysis. After the addition of the acid, the beaker is covered and heated on a sand-bath to 100° or a little above, until there seems to be no more action of the acids on the ore. The cover is then removed from the beaker, and the mixture carefully evaporated until all odor of nitric acid is expelled or white fumes of sulphur trioxide begin to appear. The action of the acids converts the lead compounds of the ore into lead sulphate. The latter is mixed, however, with other insoluble substances, such as quartz, native silicates, barium and calcium sulphates, from which it must be separated. The beaker and its contents are accordingly allowed to cool, 100 c.c. of water are then added, the mixture warmed for an hour or two, then filtered, and the insoluble matter washed with water containing a small amount of sulphuric acid. The filter and the insoluble substances upon it are then transferred to a beaker and covered with from 25 to 50 c.c. of ammonium hydrate, an excess of acetic acid is then added, and the mixture warmed and stirred for fifteen or twenty minutes. The ammonium acetate that results from the neutralization of the ammonium hydrate by the acetic acid dissolves the lead sulphate. After the mixture has been warmed and stirred for the specified time it is filtered. The filter and insoluble matters are washed with water containing some ammonium acetate to insure the complete removal of the lead sulphate. The filtrate and washings are then mixed, and the entire volume precipitated by means of hydrogen sulphide. The lead sulphide is filtered off and treated according to the directions given on page 109 for weighing it. When arsenic and antimony are present in the ore, a small quantity of the lead is liable to be left undissolved by the treatment with ammonium acetate. When, therefore, these elements are present, the insoluble residue of lead sulphate and other substances which results from the action of the mixed acids is washed with water as before, then removed from the filter by the aid of the jet from the wash-bottle, and boiled for fifteen minutes with a large excess of ten per cent. solution of sodium carbonate. By this treatment the lead sulphate is converted into lead carbonate, which is left undissolved, while the arsenic and antimony compounds dissolve in the strongly alkaline solution. The lead carbonate and other insoluble substances are thoroughly washed with hot water to remove alkali. The lead carbonate is then removed by treatment of the precipitate with warm acetic acid and subsequent washing until the washings no longer show an acid reaction. The resulting solution of lead acetate is then precipitated with hydrogen sulphide, as previously directed, and the lead sulphide treated as already outlined.

SECTION II.

ESTIMATION OF ACID RADICALS IN SIMPLE SALTS.

The estimation of free acids is done by volumetric analysis, except in some cases of mixtures of them. The estimation of acid radicals in salts is usually accomplished by gravimetric methods, although some of the radicals admit of estimation by volumetric means. When a free acid and its salts are mixed, both methods may need to be applied, in order to determine the respective amounts of free and combined acids, unless the combined acid can be estimated with a volumetric solution different from the one employed to find the amount of free acid. In all such cases the quantity of combined acid radical is found by deducting the amount of free acid radical from the total amount of acid radical present in both conditions, or by calculating it from the amount of basic radical present. When free acids are to be estimated by gravimetric analysis they are usually neutralized with sodium or potassium hydrate.

ESTIMATION OF CHLORINE IN CHLORIDES.

Solution.—Most of the metallic chlorides are soluble in water. Bismuth chloride is decomposed into bismuth oxychloride upon the addition of water, but nitric acid will dissolve this compound to a clear solution without the application of heat. The chlorine of lead chloride is brought into solution by digesting the salt with a solution of sodium bicarbonate and filtering to remove the lead carbonate. Silver chloride is mixed with three or four times its weight of sodium carbonate and the mixture heated in a porcelain crucible until it begins to fuse; water will then dissolve the sodium chloride from the metallic silver. Potassium or sodium hydrate will remove the chlorine from mercurous and mercuric chlorides, the oxides of mercury being separated by filtration.

Estimation as Silver Chloride, AgCl.—The solution is acidified with nitric acid, and silver nitrate then added until, after heating and stirring, no further precipitate is produced and a clear, supernatant liquid is obtained. The precipitate is treated by one of the methods given for the weighing of silver chloride in the estimation of silver.

The operation should be conducted as rapidly as possible, because silver chloride is decomposed by light. The chlorine of some metallic chlorides cannot be estimated by the foregoing process, since there is liability, in the presence of the metals, to incomplete precipitation in some cases, while in others precipitates of a mixed character are obtained. Examples of these behaviors are encountered in the analysis of the chlorides of chromium, antimony, tin, mercury, and platinum. The separation of the base and acid by the usual qualitative methods is the obvious remedy in such cases. Free chlorine is estimated by volumetric methods.

The combined chlorine of organic compounds is usually not precipitable by the direct addition of silver nitrate. The estimation of chlorine in such substances is most frequently done by igniting the substance with chlorine-free lime, whereby calcium chloride is formed; from this compound the chlorine may then be readily precipitated by means of silver nitrate. The ignition is conducted by introducing into a piece of combustion tube from 30 to 40 cm. long, and closed at one end, a column of lime about 5 or 6 cm. in length, then a mixture of the substance with an amount of lime equal to that in the tube, and afterwards enough lime to nearly fill the tube. The tube is then given a few taps on the table to make a passage for the gases from the organic matter along the top of the charge. It is then placed in a combustion furnace. Heat is applied to the tube in such a manner as to bring it to redness at the end of the charge next the mouth. When this is attained the heat is gradually extended towards the closed end of the tube until the whole length is at last heated to redness. The heating is then discontinued, and the tube, while still warm, but not red hot, is plunged into water contained in a beaker. Leaving the broken glass in the beaker, the contents are then acidified with nitric acid, the solution containing the calcium chloride filtered from insoluble matter, and the chlorine then precipitated with silver nitrate, as customary. The lime should be free from moisture. Fluids containing chlorine are enclosed in small glass tubes, and these embedded in the lime. Organic substances containing nitrogen should be treated with a mixture of lime and soda (soda-lime) instead of plain lime, to prevent the formation of cyanides, which would interfere in the precipitation of the chlorine with silver.

ESTIMATION OF BROMINE IN BROMIDES.

Solution.—Bromides are dissolved by the methods given for chlorides. The bromine of organic compounds is prepared for precipitation with silver nitrate by the method given for the estimation of chlorine in organic compounds.

Estimation as Silver Bromide, AgBr.—The estimation of bromine in bromides is accomplished in the same manner as the estimation of chlorine in chlorides. The precipitate of silver bromide is collected on a balanced filter, washed, and dried at 130° till the weight is constant. Free bromine is estimated like free chlorine.

ESTIMATION OF IODINE IN IODIDES.

Solution.—In most cases the metallic iodides closely resemble the corresponding chlorides and bromides in solubility. Those insoluble in water may be dissolved according to the directions given for the solution of chlorides. Free iodine is dissolved in solution of potassium iodide and estimated by volumetric analysis.

Organic compounds containing iodine are treated according to the method described for the estimation of chlorine in organic compounds. Should any iodine be set free upon treating the contents of the tube with nitric acid, sulphurous acid must be added to reduce it to hydriodic acid before the precipitation with silver nitrate is undertaken.

Estimation as Silver Iodide, AgI.—Proceed according to the method of estimating chlorides and bromides, but, before acidifying with nitric acid and applying heat, add sufficient silver nitrate to the solution to completely precipitate it. The precipitate of silver iodide is collected on a balanced filter, washed, and dried at 130° till the weight is constant.

Estimation as Palladious Iodide, PdI_2.—The following method is useful for the estimation of iodides in the presence of chlorides and bromides. Acidify the solution containing the iodide with hydrochloric acid, and add solution of palladious chloride until precipitation is completed. Set the mixture in a warm place for 24 hours, then collect the precipitate on a balanced filter, wash it with hot water till free from chlorides, and dry it to a constant weight at 100°. Or the dried palladious iodide may be ignited in hydrogen, and the iodine calculated from the palladium left in the crucible. One atom of the metal indicates two atoms of iodine.

ESTIMATION OF FLUORINE IN FLUORIDES.

Solution.—The fluorides of the alkali metals, silver, heavy metals, and earths in general are soluble in water. Those of the alkaline earths are insoluble in water, and cannot be dissolved in acids without decomposition attended with loss of fluorine.

Estimation as Calcium Fluoride, CaF_2.—If the material to be analyzed is free hydrofluoric acid in aqueous solution or a fluoride soluble in water, add sodium carbonate solution in excess and heat to boiling. If ammonia is given off, boil till all of it is expelled. If a precipitate is produced, filter the hot liquid to remove it. To the clear hot solution add calcium chloride until precipitation is complete. Allow the precipitate to subside, wash and dry it. Then ignite it in a platinum crucible (to facilitate the final washing of the calcium fluoride), allow to cool, put the crucible and contents in a porcelain dish, pour water on the mass, add acetic acid in excess, and evaporate to dryness on a water-bath, heating until the odor of acetic acid is no longer noticeable. Treat the residue of calcium acetate and fluoride with hot water, filter off the calcium fluoride, wash it free from soluble calcium salts, dry, ignite, and weigh it.

If the fluoride is insoluble in water, fuse it in a platinum crucible with six times its weight of a mixture of sodium and potassium carbonates* and twice its weight of silica. After allowing the crucible to cool, treat the fused mass with water, heat the solution with an excess of ammonium carbonate, filter off the silicic acid which precipitates, add an ammoniacal solution of zinc oxide to precipitate the silica still in solution, evaporate the mixture till all ammonia is expelled, filter, and then proceed as in the case of fluorides soluble in water.

ESTIMATION OF CYANOGEN IN CYANIDES.

Solution.—The cyanides of the alkali and alkaline earth metals and of mercury are soluble in water. The cyanides insoluble in water cannot be dissolved in acids without loss of cyanogen, but many of them may be decomposed by boiling with water and an excess of mercuric oxide, the cyanogen passing into solution as mercuric cyanide. The solution of the cyanogen of nickel cyanide and of the ferricyanides and ferrocyanides of iron may be effected in this manner. Silver cyanide can be dissolved in ammonia water.

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* For this and similar purposes the two carbonates are mixed in the proportion of their molecular weights. The advantage of such a mixture is that it fuses at a considerably lower temperature than does either carbonate singly.

Estimation as Silver Cyanide, AgCN.—The cyanogen of the cyanides of the alkalies and alkaline earths may be estimated by the method given for the determination of chlorine in chlorides, except that heat is to be altogether avoided in the precipitation with silver nitrate, which should be added in excess before the solution is acidified with nitric acid. The precipitate may be collected on a balanced filter, washed, and dried at 100° till the weight is constant; or it may be collected on a plain filter, washed, dried, transferred to a porcelain crucible, and ignited, and the resulting metallic silver weighed. One atom of silver represents one cyanogen group.

The foregoing method also serves for the estimation of free hydrocyanic acid in its commercial solutions. To determine the total cyanogen of bitter almond water, or cherry-laurel water, by a gravimetric method, precipitate the liquid with silver nitrate, then add ammonium hydrate in large excess, and immediately afterwards acidify the mixture with nitric acid. This treatment insures the precipitation of the cyanogen existing as hydrocyanate of benzaldehyde in these waters.

Silver cyanide may be dissolved and its cyanogen estimated by digesting the compound with a large excess of ammonium hydrate, in a sealed tube, at the boiling point of water, for several hours; the tube is then allowed to cool, is opened, its contents warmed to insure solution of the crystalline ammonio-cyanide of silver, the liquid filtered, if necessary, and then acidified with nitric acid to throw down the silver cyanide. This method is also applied to potassium ferricyanide and ferrocyanide.

To estimate the cyanogen in mercuric cyanide, mix the latter in aqueous solution with twice as much zinc nitrate dissolved in ammonium hydrate. Then carefully add hydrogen sulphide water to this solution until no more black precipitate is produced and the further addition of the reagent causes instead a white precipitate of zinc sulphide. Let the precipitate settle, afterwards filter, mix the filtrate which contains the cyanogen, in the form of zinc cyanide dissolved in ammonium hydrate, with silver nitrate, and, finally, acidify it with diluted sulphuric acid to precipitate the silver cyanide.

ESTIMATION OF THE ACID RADICAL IN CHLORATES.

Solution.—All the metallic chlorates are more or less readily soluble in water.

Estimation as Silver Chloride, AgCl.—Prepare a concentrated aqueous solution of the chlorate, put a piece of mossy zinc into the liquid, then add some dilute sulphuric acid to it, and set the whole aside. The hydrogen which is generated reduces the chloric acid to hydrochloric acid. When the evolution of hydrogen ceases, remove any undissolved zinc, rinse it, add the rinsings to the solution containing the hydrochloric acid, and precipitate the solution with silver nitrate. Treat the precipitate of silver chloride by one of the methods given under the estimation of chlorides.

Potassium and sodium chlorates may be converted into the corresponding chlorides by cautiously igniting them ; the residue of chloride may then be dissolved in water and the chlorine precipitated with silver nitrate. One molecular weight of silver chloride indicates the presence of one molecule of either potassium or sodium chlorate. It is obvious that the foregoing processes cannot be applied to the estimation of chlorates when chlorides are present, unless the latter be estimated in a portion of the original material, and the weight of silver chloride obtained in the estimation of the chlorate corrected by deducting from it the quantity due to chloride. Hypochlorites are estimated by volumetric analysis.

ESTIMATION OF SULPHUR IN SULPHIDES.

Solution.—The sulphides of the alkali and alkaline earth metals are soluble in water ; the sulphides of the other metals dissolve in hydrochloric, nitric, or nitrohydrochloric acid, but not, as a rule, without loss of sulphur. The sulphur of organic substances may be oxidized to sulphur trioxide and brought into solution as alkali sulphate by heating with a mixture of pure anhydrous sodium carbonate and pure potassium chlorate in a glass combustion tube sealed at one end. The mixture of the salts is composed of 8 parts of sodium carbonate and 1 part of potassium chlorate. The charging and heating of the tube is conducted according to the method given for the estimation of chlorine in chlorides. After the carbon is completely consumed and the ignition is completed, the hot tube is put in water, the insoluble matter removed by filtration, and the sulphates precipitated with barium chloride, as described in the estimation of the acid radical in sulphates. The oxidation of the sulphur in some organic compounds may be effected by heating the substances with solution of potassium hydrate, and passing chlorine into the liquid. When oxidation is complete, the solution is acidified with hydrochloric acid and evaporated to dryness; the residue is dissolved in water, and the resulting solution precipitated with barium chloride as usual.

Estimation as Barium Sulphate, $BaSO_4$.—The following methods are applicable to solid sulphides only; for the estimation of hydrogen sulphide in solution, see water analysis, page 301.

The estimation of sulphur in the sulphides of those metals which form soluble sulphates is conveniently done as follows. Warm the finely pulverized metallic sulphide on a water-bath with nitric acid of 1.36 sp. gr., and add small quantities of potassium chlorate at a time to the heated mixture until all of the sulphur disappears. Then remove the excess of potassium chlorate by repeatedly evaporating to dryness with hydrochloric acid; finally, see that the solution contains some free hydrochloric acid, and precipitate it with barium chloride, according to the method given on page 119 for the estimation of sulphates. Calculate one atom of sulphur for each molecular weight of barium sulphate found.

For the estimation of sulphur in lead sulphide,—or other sulphides which the foregoing treatment would convert into insoluble sulphates,—mix the finely pulverized sulphide in a platinum crucible with six times its weight of dried sodium carbonate and four times its weight of potassium nitrate by stirring with a glass rod. Guard against loss in removing the rod, carefully heat the crucible until its contents fuse, prolong the fusion for half an hour, allow the crucible to cool, treat the mass with hot water, filter, and wash all sulphates into the filtrate. Then free the filtrate from nitrates by repeated evaporations with hydrochloric acid, and precipitate it with barium chloride. If the sodium carbonate contains any sulphate as an impurity, a correction must be made for its amount.

These methods estimate all of the sulphur in sulphides, and are, therefore, useless for the estimation of the true sulphide in sulphurated lime and sulphurated potassa, which are liable to contain sulphate, thiosulphate, and even free sulphur. The United States Pharmacopœia requires these substances to respond to the following tests:

"If 1 gm. of sulphurated lime be gradually added to a boiling solution of 2.08 gm. of cupric sulphate in 50 c.c. of water, the mixture digested on a water-bath for fifteen minutes, and filtered when cold, no color should be imparted to the filtrate by 1 drop of potassium ferrocyanide test-solution (presence of at least 60 per cent. of pure calcium monosulphide)."

"On triturating 1 gm. of sulphurated potassa with 1 gm. of crystallized copper sulphate and 10 c.c. of water, and filtering, the filtrate should remain unaffected by hydrogen sulphide test-solution, corresponding to at least 12.85 per cent. of sulphur combined with potassium to form sulphide."

In the foregoing tests the copper of the copper sulphate is entirely converted into insoluble copper sulphide if the sulphurated compounds are of the required strengths. The tests applied to the filtrates are for the purpose of ascertaining if all of the copper has been rendered insoluble in this manner.

ESTIMATION OF THE ACID RADICAL IN SULPHITES.

Solution.—The sulphites and bisulphites of the alkali metals are soluble in water. These are the most important members of this class of salts. Sulphites insoluble in water are decomposed by boiling with sodium carbonate, which effects solution of the radical in the form of sodium sulphite.

Estimation as Barium Sulphate, $BaSO_4$.—Pour the solution of the sulphite into an excess of chlorine or bromine water, mix well, and after a few minutes warm the solution to expel the remaining excess of chlorine or bromine. Then precipitate the solution with barium chloride, and treat the barium sulphate as directed in the estimation of sulphates. A molecular weight of barium sulphate represents a molecular weight of SO_2 or SO_3. As sulphites are prone to change to sulphates, an allowance must be made for any sulphate in the salt. Sulphites are usually estimated by volumetric methods.

ESTIMATION OF THE ACID RADICAL IN SULPHATES.

Solution.—Most of the sulphates dissolve in water, the important exceptions being those of barium, strontium, calcium, mercury, and lead. The sulphuric acid of the barium, strontium, and calcium salts may be brought into solution by fusing the powdered substance in a platinum crucible with five times its weight of a mixture of sodium and potassium carbonates, and washing out the alkali sulphates and carbonates of the mass with hot water. Mercuric sulphate is decomposed by water into a basic salt; the latter, however, is soluble in hydrochloric acid. Mercurous sulphate is dissolved by oxidizing it to the mercuric state, which is done by heating the salt with hydrochloric acid and adding potassium chlorate. The acid radical of lead sulphate may be made to go into solution by digesting the salt at the ordinary temperature with a solution of sodium or potassium bicarbonate, the insoluble lead carbonate being removed by filtration.

Estimation as Barium Sulphate, $BaSO_4$.—The solution should be free from nitrates and chlorates, which may be removed by repeatedly evaporating the solution with hydrochloric acid. The solution is finally left acid with hydrochloric acid and diluted well with water. It is then boiled, and barium chloride added until no further precipitate is produced. The precipitate of barium sulphate is treated exactly as in the estimation of barium, except that it must be washed till free from chlorides.

If the alkali carbonate used in bringing about the solution of the sulphate contained any alkali sulphate, the result will need to be corrected for the amount of barium sulphate which this has yielded.

ESTIMATION OF THE ACID RADICAL IN THIOSULPHATES.

Solution.—Thiosulphuric acid is not known in the free state, but only in combination in certain salts, of which sodium thiosulphate is the most important. It is soluble in water.

Estimation as Barium Sulphate, $BaSO_4$.—Proceed to obtain the barium sulphate exactly as in the estimation of sulphites in the form of barium sulphate. Two molecules of barium sulphate correspond to one molecule of sodium thiosulphate. It is evident that this method of estimating thiosulphates is not possible without interference when sulphates, sulphites, or sulphides are present. When sulphates, the usual impurities of thiosulphates, are present a correction must be made in the quantity of barium sulphate found; or, what is better, the thiosulphate may be estimated by a volumetric process in which sulphates do not interfere.

ESTIMATION OF THE ACID RADICAL IN NITRATES.

Solution.—All nitrates are soluble in water; bismuth nitrate, however, is decomposed by the addition of much water, with the formation of an insoluble basic nitrate. As nitric acid cannot be precipitated from its solutions, it must be estimated in some indirect way, when done by gravimetric analysis.

Estimation as Nitrogen Pentoxide, N_2O_5.—The following example will serve to illustrate the estimation of the acid radical in nitrates, when moisture, organic matter, ammonium salts, mercury, and other volatile substances are absent:

Potassium nitrate is fused at as low a temperature as possible in a platinum crucible, and poured out on a porcelain surface to cool.

About 3 grammes of finely powdered silica are heated in a crucible, and, after cooling, weighed. About 1 gramme of the finely powdered potassium nitrate is mixed with the silica in the crucible, the mixture brought to a dull red heat for half an hour, allowed to cool, and weighed. The heating is repeated until the weight is constant. The loss indicates the amount of N_2O_5, and from this the amount of NO_3 which was present can be calculated. Sulphates and chlorides are not decomposed at this temperature.

All nitrates may be estimated by distilling them in a retort with sulphuric acid to liberate the acid radical, collecting the latter in standard alkali solution, determining the number of c.c. of alkali which the distillate has neutralized by titrating with standard acid solution, and from this amount calculating the quantity of acid radical present. The weighed nitrate is introduced through the tubulure of the retort, the neck of which has previously been attached to a receiver containing the standard alkali solution. Upon the nitrate in the retort is poured a cooled mixture of sulphuric acid and water; the tubulure is then closed, and the retort heated on a sand-bath to 170°. For each gramme of potassium nitrate, or its equivalent, 5 c.c. of concentrated sulphuric acid and 10 c.c. of water are used; and, for the same quantity, the distillation is carried on for three hours. The time required for the operation may be shortened by conducting the distillation *in vacuo*, under which conditions a water-bath heat will suffice. If chlorides are present, they must be removed by means of silver sulphate or oxide before the nitrate is treated with sulphuric acid, or hydrochloric acid will distil over and vitiate the result.

ESTIMATION OF THE ACID RADICAL IN HYPOPHOSPHITES.

Solution.—All the important hypophosphites are soluble in water.

Estimation as Mercurous Chloride, Hg_2Cl_2.—If the aqueous solution of a hypophosphite be poured into an excess of solution of mercuric chloride and the mixture acidified with hydrochloric acid and warmed, a precipitate of mercurous chloride will fall. The mixture is kept on a boiling water-bath for about an hour. The mercurous chloride is collected on a balanced filter, washed, dried at 100°, and weighed. The filtrate should be boiled to make sure that precipitation is complete. Ferric hypophosphite is dissolved in water by the aid of citric acid. The solution so obtained is made alkaline with ammonium hydrate to decompose the ferric compound; most, if not all, of the resulting ferric hydrate dissolves on account of the ammonium citrate present. After ten minutes the alkaline solution is mixed with the solution of mercuric chloride and the whole acidified with hydrochloric acid and heated in the manner described. Two molecular weights of mercurous chloride represent one molecular weight of hypophosphorous acid, or an equivalent amount of hypophosphite. This acid and its salts are usually estimated by volumetric analysis.

ESTIMATION OF THE ACID RADICAL IN ORTHOPHOSPHATES.

Solution.—The orthophosphates of the alkali metals are soluble in water, with the exception of lithium phosphate; this and the other orthophosphates dissolve in hydrochloric or nitric acid.

For the estimation of the total phosphorus in an organic substance, the material is ignited with sodium carbonate and potassium chlorate as described in the estimation of sulphur in sulphides. The phosphorus is oxidized to phosphorus pentoxide by this treatment; the latter is then estimated by the usual methods, and the phosphorus calculated from its amount.

Estimation as Magnesium Pyrophosphate, $Mg_2P_2O_7$.—If the phosphate is soluble in water, add to its aqueous solution enough ammonium hydrate to neutralize it, or make it decidedly alkaline; follow this with some ammonium chloride solution, and then precipitate with a slight excess of magnesia mixture. Finally, add to the mixture one-third its volume of ammonium hydrate, mix well without rubbing the beaker with the rod, and set the whole aside for 12 hours, to allow the precipitate of magnesium ammonium phosphate to completely separate. At the expiration of the specified time pour the clear, supernatant liquid on a filter, and treat the precipitate of magnesium ammonium phosphate as described under the estimation of magnesium.

The preceding method is inapplicable to the phosphates which require acid to dissolve them, since, upon making the solution alkaline with ammonium hydrate, the original phosphates are precipitated. To estimate a member of this class of phosphates, it is customary to separate the phosphorus pentoxide from the metal with which it is combined, in order that it may be brought into alkaline solution for precipitation with magnesia mixture. This separation is accomplished by precipitating the acid solution of the phosphate with ammonium molybdate; the ammonium phosphomolybdate, $(NH_4)_3PO_4(MoO_3)_{12}$, which is thrown down by this reagent, is dissolved in ammonium hydrate, and the alkaline solution so obtained precipitated with magnesia mixture as in the case of phosphates soluble in water. The solution of the phosphate to be treated in this manner should be made in nitric acid; it should contain little or no hydrochloric acid or chlorides, and should be free from organic substances, such as tartaric, citric, and oxalic acids. It is not necessary to remove silicic acid by evaporating the nitric acid solution to dryness before precipitating with the ammonium molybdate. The presence of ammonium nitrate in the solution overcomes the tendency of other salts to interfere with the reaction, and has a desirable effect in general upon the precipitation. The operation is conveniently conducted as follows:

About 0.100 gramme of the phosphate is dissolved in nitric acid, the solution neutralized with ammonium hydrate until a precipitate just begins to form, 5 c.c. of nitric acid of sp. gr. 1.4 added, then 10 c.c. of a saturated, aqueous solution of ammonium nitrate, and afterwards enough water to make the solution measure 50 or 75 c.c. Heat is now applied and the solution brought to a full boil. It is then removed from the lamp, no more heat being applied, and treated at once with 5 c.c. of a 9 per cent. aqueous solution of ammonium molybdate, the phosphate solution being stirred as the reagent is added.* The

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* The reaction may be expressed as follows:

$$Ca_3(PO_4)_2 + 24(NH_4)_2MoO_4 + 48HNO_3 = 2((NH_4)_3PO_4.(MoO_3)_{12}) + 3Ca(NO_3)_2 + 42NH_4NO_3 + 24H_2O.$$

mixture is now allowed to rest quietly for about one minute, during which time the precipitate settles almost completely. More ammonium molybdate solution is added to the clear, supernatant liquid, in successive portions of about 5 c.c., until precipitation is completed. The clear solution is then decanted to a filter, the precipitate washed a few times with water by decantation, then transferred to the filter, and washed till the washings are free from acid.* The precipitate is then dissolved by pouring over it on the filter ammonium hydrate mixed with three times its volume of water, care being taken that the filter is thoroughly washed with this solution. Hydrochloric acid is added to the filtrate and washings till the liquid is not quite neutral, but still retains a decided alkaline reaction. This solution is then precipitated with magnesia mixture according to the directions for phosphates soluble in water. Or the precipitate of ammonium phosphomolybdate may be treated by a volumetric process given hereafter. The method of precipitating with ammonium molybdate just given is not applicable in its exact details to phosphates containing iron and aluminum; it is, however, especially well suited for calcium and magnesium phosphates. A method that is well fitted for the estimation of the phosphoric acid radical in the presence of iron and aluminum, and, therefore, applicable to the estimation of phosphorus pentoxide in "phosphate rock" used for fertilizing purposes, consists in mixing the hydrochloric acid solutions of the phosphate with an alkaline solution of magnesium citrate, by which the phosphoric radical is precipitated in the form of magnesium ammonium phosphate, and this subsequently converted into magnesium pyrophosphate by ignition. If the phosphate is contaminated with silicates decomposable by hydrochloric acid, the silica must be removed before adding the magnesium citrate solution. Its removal is effected by evaporating the acid solution to dryness, treating the residue with water acidulated with hydrochloric acid, and filtering off the insoluble silica. The alkaline solution of magnesium citrate is prepared by dissolving 27 grammes of magnesium carbonate in a solution of 270 grammes of citric acid in 350 c.c. of warm water; after effervescence ceases and the solution is cool, 400 c.c. (or a decided excess) of 10 per cent.

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* The filtrate and washings from the yellow precipitate give on standing a snow-white precipitate of molybdic acid, showing that all of the phosphorus pentoxide has been precipitated. When silica is not removed, the filtrate from the yellow precipitate has a yellow tinge.

ammonium hydrate are added, and the whole diluted with water to a liter. Some of this reagent is added to the hydrochloric acid solution of the phosphate, and the liquid then made alkaline with a large excess of ammonium hydrate. If the quantity of magnesium citrate solution used is sufficient, no precipitate will form until a few minutes elapse. Should a precipitate fall immediately after the addition of the ammonium hydrate, it is likely to contain iron or aluminum phosphate; in the event of one forming under these circumstances, the operation is repeated, using twice as much alkaline solution of magnesium citrate as before. When the precipitation takes place in the proper manner, the vessel is allowed to stand 12 hours; the precipitate of magnesium ammonium phosphate is then collected and prepared for weighing, as magnesium pyrophosphate, by the treatment usually given it.

Instead of converting the precipitate of ammonium phosphomolybdate into magnesium pyrophosphate as previously described, the phosphorus pentoxide may be conveniently estimated by a volumetric method involving the titration of the thoroughly washed precipitate with a standard solution of potassium hydrate. The latter is prepared by diluting 323.7 c.c. of normal potassium hydrate volumetric solution to one liter with water. A standard acid solution also is needed; it may be made by diluting 323.7 c.c. of normal oxalic or sulphuric acid volumetric solution to one liter. Phenol-phtaleïn test-solution should be used as the indicator for standardizing these solutions. The process is performed by transferring the thoroughly washed filter and precipitate of ammonium phosphomolybdate to a beaker, running in the standard alkali solution during constant stirring until the precipitate is dissolved, which is indicated by the disappearance of its yellow color,* adding at least a dozen drops of phenolphtaleïn test-solution, and then titrating the contents of the beaker with the standard acid solution until the pearly color disappears and the solution is colorless. The presence of the filter paper does not interfere with the accuracy of the titration. After deducting the volume of the acid solution used from that of the alkali solution, the remainder gives the percentage of phosphorus

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* The potassium hydrate reacts with the ammonium phosphomolybdate to form soluble ammonium phosphate, ammonium molybdate, and potassium molybdate, as shown by the following equation:

$$2((NH_4)_3PO_4.(MoO_3)_{12}) + 46KOH = 2(NH_4)_2HPo_4 + (NH_4)_2MoO_4 + 23K_2MoO_4 + 22H_2O.$$

pentoxide, P_2O_5, directly, each c.c. being equal to 1 per cent. of P_2O_5, when 0.100 gramme of the phosphate is taken for analysis.

In all of these methods the presence of arsenates must be guarded against.

ESTIMATION OF THE ACID RADICAL IN PYROPHOSPHATES.

Solution.—The phosphates of the alkalies are soluble in water; those of other bases are mostly insoluble in water, but soluble in acids.

Estimation as Magnesium Pyrophosphate, $Mg_2P_2O_7$.—Pyrophosphates are determined by converting them into orthophosphates, and then proceeding as in the estimation of the acid radical in the latter class of salts.

The conversion of the alkali pyrophosphates is effected by fusing the dry material with about 5 times its weight of a mixture of sodium and potassium carbonates for 1 or 2 hours; the pyrophosphates of the alkaline earths are changed by boiling their solutions with one-fourth their volume of nitric or sulphuric acid for an hour or two. In case the first treatment is applied, the fused mass is dissolved in water, and the solution treated with magnesia mixture, according to the method of estimating orthophosphates soluble in water, while in the event of the second method of conversion being used, the solution is filtered from any insoluble substance, the latter washed, and the filtrate and washings treated either by the ammonium molybdate or the alkaline magnesium citrate method for the precipitation of the phosphorus pentoxide.

ESTIMATION OF THE ACID RADICAL IN METAPHOSPHATES.

Solution.—The metaphosphates resemble the pyrophosphates in solubility; those insoluble in water dissolve in nitric or hydrochloric acid.

Estimation as Magnesium Pyrophosphate, $Mg_2P_2O_7$.—The estimation of metaphosphates is conducted exactly as in the case of pyrophosphates.

ESTIMATION OF THE ACID RADICAL IN BORATES.

Solution.—The borates of the alkali metals are soluble in water; the other borates are either insoluble in water or only very sparingly soluble in it. The acid radical of borates insoluble in water may be brought into solution as alkali borate by boiling them with potassium hydrate and filtering off the precipitated base.

Estimation as Potassium Borofluoride, KBF_4.—The estimation of the acid radical in borates presents many difficulties. Of the various methods of analysis which have been proposed, the following is probably the one best suited to the direct determination of the boron trioxide in the alkali borates. If other borates are to be estimated by this method the boric acid must be converted into potassium borate. Put the solution of the borate in a platinum vessel, add to it twice as much potassium hydrate in solution as is necessary to form potassium borate with all of the boric acid present, then add hydrofluoric acid in excess, and evaporate the mixture to dryness on a water-bath. If sufficient hydrofluoric acid has been added, the vapor from the evaporating liquid will turn blue litmus paper red; if this change does not occur, more hydrofluoric acid must be added. Warm the dry residue with a 20 per cent. aqueous solution of potassium acetate for half an hour, then allow the mixture to cool; after 12 hours decant the liquid upon a balanced filter, wash the precipitate of potassium borofluoride by decantation, and finally on the filter with solution of potassium acetate until a test with calcium chloride shows that all hydrogen potassium fluoride has been removed. When this is found to be the case, wash the filter and precipitate with 80 per cent. alcohol to remove potassium acetate, then dry at 100°, and weigh. Test the weighed salt for potassium silicofluoride by dissolving it in boiling water, adding ammonium hydrate in excess, and evaporating to dryness; repeat this entire treatment five or six times, then, after dissolving and adding ammonium hydrate, filter off any insoluble silicic acid, evaporate the filtrate to dryness, wash the residue with potassium acetate solution and alcohol as previously directed, dry the pure potassium borofluoride, and weigh it.

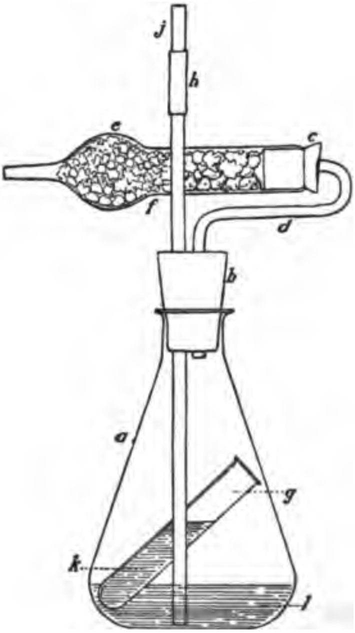
ESTIMATION OF THE ACID RADICAL IN CARBONATES.

Solution.—The carbonates of the alkalies, with the exception of lithium, are soluble in water; the other carbonates are insoluble in water. All carbonates are decomposed by acids with liberation of carbon dioxide, those insoluble in water dissolving by this treatment, when the base present forms a soluble salt with the acid used.

Estimation as Carbon Dioxide, CO_2.—The estimation of the acid radical in carbonates is sometimes done by igniting a weighed quantity of the substance until it ceases to lose weight, the loss being taken as carbon dioxide. But for this method to succeed the carbonate must, of course, be decomposable by heat, and other volatile substances (such as water, both adhering and combined) must be absent. The requirements of this method, therefore, preclude the estimation of the alkali carbonates and bicarbonates, ammonium carbonate, and the basic carbonates of lead, magnesium, and zinc, by such means. Calcium carbonate may, however, be so estimated.

A method of estimation that is adapted to nearly all cases consists in treating the carbonate with dilute acid and taking the loss as carbon dioxide. This method, like the preceding one, is obviously inaccurate where other gases or vapors are evolved by the action of the acid, unless suitable precaution be taken to prevent their escape from the apparatus in which the decomposition is made to take place. Any one of the numerous designs of apparatus offered by chemical instrument makers for this purpose may be employed, but that known as Schroetter's is probably the best. A convenient and inexpensive form is shown in Fig. 7. The illustration discloses the arrangement of the apparatus, which consists of a small Erlenmeyer flask, *a*; the rubber stoppers, *b* and *c*; the bent glass tube, *d*; the drying tube, *e*, filled with calcium chloride; the straight glass tube, *f*; and the small test-tube, *g*. The upper end of the straight tube is closed with a short section of rubber tubing, *h*, into one end of which has been slipped a plug of glass rod, *j*. The operation is conducted as follows. The small test-tube is removed from the flask, filled two-thirds full with acid, *k*, and carefully put back into the flask by means of forceps, taking care not to spill the acid into the flask; some cold water, *l*,

FIG. 7.



is then forced into the flask from the wash-bottle, the rubber stopper, *b*, to which the remaining parts of the apparatus are attached as illustrated, is then reinserted as shown in the accompanying figure. The apparatus and its contents are then weighed. They are then taken from the balance, the stopper, *b*, removed from the neck of the flask just sufficiently to admit of the introduction of the end of a dry funnel, but not far enough to remove the wet end of the straight tube from the flask. A suitable quantity of the carbonate is then transferred to the flask through the dry funnel in such a way that none of it falls into the test-tube containing the acid. The stopper, *b*, is then replaced in the neck of the flask, and the apparatus again weighed with its contents. The gain in weight which results from the addition of the carbonate shows, of course, the exact amount of carbonate put into the flask. After the weighing the apparatus is again removed from the balance, and inclined so that the acid may flow out of the test-tube and come into contact with the carbonate. The carbonate is decomposed by the acid; effervescence occurs from the escaping carbon dioxide, which passes out of the flask through the bent tube, *d*, and is deprived of moisture by the calcium chloride in the drying tube, *e*, before it escapes from the apparatus. When effervescence abates, the glass plug is removed from the straight tube, a piece of rubber tubing is attached to the open end of the drying tube, *e*, and bubbles of air slowly drawn through the apparatus, to displace the heavier carbon dioxide, by sucking on the free end of the rubber tubing. After a dozen or more bubbles have been drawn through the liquid, *l*, the rubber tubing is detached, the glass plug replaced, and the apparatus balanced; afterwards suction and weighing are alternately repeated in the foregoing manner until the apparatus ceases to lose weight. The total loss in weight is the amount of carbon dioxide yielded by the quantity of carbonate taken. Hydrochloric acid is usually used to decompose the carbonate, but sulphuric or nitric acid may be preferable in some cases. Care must be taken during the operation to have the apparatus dry on the outside and to lose no liquid. In cases which require great accuracy, the carbon dioxide is drawn through a solution of potassium hydrate contained in a weighed bulb apparatus; the alkali absorbs and retains the carbon dioxide; hence the quantity of the latter may be estimated by noting the increase in weight of the potash bulb. Where this last method is employed, a calcium chloride tube must be interposed between the flask in which the carbon dioxide is generated and the potash bulb, in order to prevent moisture from passing into the latter and thus vitiating the result. It is customary to warm the flask when carbon dioxide is estimated in this manner.

The alkali carbonates and bicarbonates are usually determined volumetrically. For the determination of free carbon dioxide in aqueous solution, see water analysis.

ESTIMATION OF THE ACID RADICAL IN SILICATES.

Solution.—The silicates of potassium and sodium, the so-called soluble or water glasses, are soluble in water. The remaining silicates are insoluble in water; some of them can be dissolved in acids, but not without undergoing a decomposition resulting in the separation of silicic acid. As a rule, silicates are divided into two classes, those which are decomposed by acids with separation of silicic acid and solution of their basic radicals, and those which require fusion with alkali carbonates, for the purpose of forming alkali silicates, before silicic acid can be separated and the basic radicals dissolved by treatment with acids. The silicates of potassium and sodium and many native silicates belong to the first class; the second class includes most of the native silicates.

When an aqueous solution of an alkali silicate is treated with an acid, the silicic acid which is liberated remains dissolved in the water, unless the solution contains much alkali salts. This soluble silicic acid is supposed to have the formula H_4SiO_4. But by heating the solution, or by concentrating it by evaporation, the silicic acid of the said composition parts with water to form H_2SiO_3 (or other hydrates of SiO_2), which is coagulated and rendered permanently insoluble in water and acids; this is especially true if the evaporation is carried to dryness, when a pulverulent form of hydrated silica is obtained. By ignition, all the forms of precipitated silicic acid lose water and are converted into amorphous silicon dioxide.

Estimation as Silicon Dioxide, SiO_2.—The separation of silicic acid from the basic radicals and its estimation as silicon dioxide is almost always accomplished by one or other of the methods about to be described. When the silicate is completely decomposable by acids, a weighed quantity of the very finely powdered substance is placed in a porcelain dish and covered with concentrated hydrochloric acid, unless silver or lead is present, when nitric acid is to be used. The mixture is then gently heated on the water-bath, and stirred with a glass rod having a rounded end, until decomposition is complete, which is known to be the case when no more grittiness can be felt with the rod anywhere in the dish. When this condition is attained the mixture is evaporated to dryness on the water-bath, and the residue heated until thoroughly dry and acid fumes no longer escape. During the drying any lumps should be crushed with the glass rod. Sometimes it may be necessary to moisten the dry mass with water and evaporate again. The dry residue is well moistened with hydrochloric acid, the mixture warmed on a water-bath, treated with half a dishful of hot water, and allowed to settle. The supernatant liquid is then poured through a filter, the residue of silicic acid is again treated with hydrochloric acid, warmed, diluted with water, this decanted as before, the entire treatment of the residue repeated a third time, the residue transferred to the filter, washed with hot water, thoroughly dried, and ignited. The product of ignition is silicon dioxide.

The basic radicals may be estimated in the filtrate from the silicic acid by the directions given elsewhere for the analysis of silicates. If the silicate is decomposable by hydrochloric (or nitric) acid, it is reduced to an impalpable powder (that does not grit between the teeth), mixed in a platinum crucible with about four times its weight of anhydrous sodium carbonate, by stirring with a short glass rod rounded at the end ; the rod is rolled in some more sodium carbonate on a piece of glazed paper, this carbonate transferred to the crucible and evenly spread over the top of the contents. The lid is then placed on the crucible and heat applied with a Bunsen burner. At first just sufficient heat is employed to cause the contents of the crucible to agglutinate, and thus allow the carbon dioxide to escape without producing spirting. After a few minutes the heat is gradually increased to bright redness and maintained at that point until the contents of the crucible are fusing quietly, without effervescence. When this is found to be the case, the heat is continued for 20 minutes. The red-hot crucible is then set on a cold iron plate, to chill it rapidly as an aid in removing the fused mass ; when cold the crucible is given a rolling motion between the thumbs and forefingers to loosen the contents, which may then be removed in the form of a cake. This cake is put into a porcelain dish, the latter half filled with water, the mixture warmed, and hydrochloric (or nitric) acid added in small portions, during cautious stirring, until the cake is disintegrated, effervescence ceases, and the mixture has an acid reaction. Should any of the fused mass adhere to the crucible and not be removed with the cake, the crucible is put into the dish along with the cake ; when the material is loosened from the sides of the crucible the latter is removed and the liquid adhering to it washed back into the dish with water. The dish is kept covered with a watch-glass, during the treatment of the fused mass with water and acid, to prevent loss of material through effervescence ; the acid may be added from a pipette or glass tube inserted in the lip of the dish. After effervescence ceases, any liquid which has collected on the watch-glass is washed into the dish. The operation is known to be successful if no gritty particles can be felt with the glass rod. If such particles are present, the whole process should be repeated with a more finely pulverized portion of the silicate.

The contents of the dish are now evaporated to dryness on the water-bath, and from this stage treated exactly as in the case of silicates decomposable by acids. Instead of sodium carbonate, a mixture of sodium and potassium carbonates (which fuses more readily than the former) may be used to decompose the silicate.

In the case of mixed silicates, partly decomposable by hydrochloric acid and partly undecomposable by it, the fusion with sodium carbonate and subsequent treatment with hydrochloric acid may be resorted to at once, without preceding it by the simple treatment with hydrochloric acid. All of the silica is obtained by this procedure. The purity of the weighed silica should always be tested. This may be done by warming a portion of the silica on a water-bath with a strong solution of sodium carbonate for an hour in a platinum vessel. The silica will dissolve if pure ; if it does not completely dissolve, weigh the reserved portion of silica, fuse it with sodium carbonate as directed for silicates undecomposable by acids, separate the silicic acid as described in the same place, and correct the result for the total quantity of impure silica. Pure silica should leave no residue when evaporated in a platinum vessel with an excess of hydrofluoric acid and a few drops of sulphuric acid.

Analysis of Silicates.—The metals which most commonly occur in silicates are iron (both in the ferrous and ferric condition), aluminum, manganese, calcium, magnesium, potassium, and sodium. The analysis of a silicate may therefore render the separation and determination of all of these constituents necessary. Thus the complete analysis of a silicate for these substances will offer an opportunity of learning the manner in which several bases are separated from one another. For the details of the methods involved, the operator is referred to the estimations of silicic acid and the various basic radicals. The analysis is begun by decomposing the silicate with hydrochloric acid or sodium carbonate as in the estimation of silicic acid; the method of fusing with sodium carbonate and subsequently treating with hydrochloric acid is generally used for this purpose, even in the case of mixed silicates, partly decomposable by hydrochloric acid and partly undecomposable by it. The silicic acid is collected, washed, ignited, and weighed as silicon dioxide. The filtrate from the silicic acid contains the metals as chlorides; it is boiled with some hydrochloric and nitric acids to insure the oxidation of any ferrous iron. The method of separating iron and aluminum to be applied to this filtrate depends upon the absence or presence of manganese. If manganese is present in the silicate, it will impart the green color of sodium manganate to the mass got by fusing the silicate with sodium carbonate, and thus make known its presence. When this color is not obtained, the filtrate, after oxidation of the iron, is mixed with ammonium chloride to prevent the precipitation of magnesium, and afterwards made alkaline with ammonium hydrate to precipitate the iron and aluminum as hydrates. The precipitate is washed, dissolved in hydrochloric acid, and the solution evaporated to expel excess of acid; the residue is taken up with water, and a large excess of potassium hydrate added to the solution, for the purpose of precipitating the iron as ferric hydrate and holding the aluminum in solution as potassium aluminate. The ferric hydrate is washed, ignited, and weighed as ferric oxide. The filtrate containing the potassium aluminate is acidified with hydrochloric acid and then warmed with an excess of ammonium hydrate to precipitate the aluminum. The aluminum hydrate is washed, ignited, and weighed as aluminum oxide. Sometimes the precipitate of ferric and aluminum hydrates is washed, ignited, and weighed as mixed oxides, these dissolved either in hot hydrochloric acid or by fusion with potassium bisulphate and treatment with dilute sulphuric acid, the iron estimated volumetrically, and the aluminum calculated by difference. The filtrate from the precipitate of ferric and aluminum hydrates is treated with ammonium oxalate to precipitate the calcium as oxalate; this is washed, ignited, and weighed as calcium oxide. Magnesium is thrown down in the filtrate from the calcium oxalate by means of ammonium phosphate. The precipitate of magnesium ammonium phosphate is washed, ignited, and weighed as magnesium pyrophosphate, which is calculated into magnesium oxide. When manganese is present, the iron and aluminum cannot be precipitated in a pure condition by means of ammonium hydrate, since manganese is also precipitated by this reagent, and on account of the ease with which manganous hydrate changes to manganic hydrate is liable to be left undissolved by the excess of the precipitant. Therefore in the presence of manganese, the iron and aluminum are precipitated as basic acetates by the method given for the precipitation of iron in that form under the estimation of this metal as ferric oxide. If but little iron is present, add twice as much sodium acetate in this precipitation as ordinarily. After the precipitate is washed it is dissolved, and the iron and aluminum are separated from each other by an excess of potassium hydrate, as already outlined. The manganese is precipitated in the filtrate from the basic acetates, after the addition of ammonium chloride, either in the form of manganese dioxide or manganous sulphide, according to the directions given under the estimation of manganese. Unless known to exist in the silicate in a higher state of oxidation, the manganese is calculated into manganous oxide. After expelling the excess of chlorine or bromine by heat, the calcium and magnesium are separated from the filtrate from the manganese precipitate by the methods employed when manganese is absent.

Potassium and sodium are estimated in a fresh portion of the silicate. For this purpose about 1 gramme of the powdered silicate is thoroughly mixed in a platinum crucible with an equal weight of ammonium chloride and about eight times as much calcium carbonate. The stirring rod is wiped against some calcium carbonate on a piece of glazed paper, and this salt put into the crucible on top of the mixture. The crucible is then cautiously heated with a Bunsen burner flame until no more white fumes of ammonium salts are given off. The lower three-fourths only of the crucible are then brought to a red heat and maintained in this condition from 40 to 60 minutes. This heat just suffices to agglutinate the mass, which contracts in volume but does not liquefy. Should the mass fuse, the operation is to be repeated, using more calcium carbonate; otherwise difficulty will be experienced in the subsequent treatment of the mass with water. The reaction results in the formation of chlorides of potassium and sodium. After the specified time the crucible is allowed to cool; the mass is then removed and boiled, in a covered dish, with water until it is disintegrated. If any of the mass adheres to the crucible, the latter must be put into the dish and left there until the hot water removes the adhering substances. After half an hour or so the solution is decanted upon a filter, any coarse, granular portions of the residue crushed with a glass rod or pestle, the residue again boiled with water, and a second decantation made. When complete disintegration of the mass has been effected, the insoluble matter is transferred from the dish to the filter and washed with water until the washings acidified with nitric acid give no turbidity with silver nitrate. The filtrate and washings now contain all of the potassium and sodium chlorides, and, in addition thereto, hydrate and chloride of calcium. The calcium is precipitated in the filtrate by the addition of ammonium carbonate, and without filtering to remove the calcium carbonate, the mixture is evaporated in a porcelain dish to a small bulk. More ammonium carbonate is then added, and the mixture boiled and poured upon a small filter. The filtrate is collected in a platinum vessel, evaporated to dryness on a water-bath, and the residue ignited to expel ammonium chloride. The contents of the vessel are then treated with a small quantity of water, a few drops of ammonium carbonate solution added to precipitate the last traces of calcium, the mixture poured upon a small filter, the filtrate evaporated in a platinum vessel to dryness as before, and the residue heated to incipient fusion. The crucible is then allowed to cool, and its contents weighed as potassium and sodium chlorides. The potassium and sodium are separated from each other by means of platinic chloride, as described under the estimation of potassium in its salts; the amount of sodium is found by difference. Both metals are calculated into oxides.

Ferrous iron is determined by volumetric analysis. The pulverized silicate is heated with a mixture of 4 parts sulphuric acid and 1 part water in a sealed tube for 2 hours at 210°. The tube is then opened, its contents rinsed into a beaker with water, and titrated with decinormal potassium permanganate volumetric solution. The ferrous iron found in this manner is calculated into ferrous oxide. An amount of metallic iron equivalent to this ferrous oxide is deducted from the total metallic iron indicated by the ferric oxide obtained in the gravimetric analysis of the silicate, and the remainder calculated into ferric oxide.

If, for any reason, it is desirable to separate the bases of the portion of a mixed silicate decomposable by hydrochloric acid from those of the other portion, the decomposition with hydrochloric acid is first carried out on a weighed quantity of the material and the soluble matter removed by filtration ; the insoluble residue of silicic acid and undecomposed silicate which remains from this treatment is then fused with sodium carbonate to decompose the unaltered silicate. All of the silicic acid is obtained upon treating the fused mass with acid. Crum's test for manganese should be applied to the solution of the bases from the silicate decomposable by acid before undertaking the analysis.

Many silicates contain water. In the absence of ferrous iron and other constituents which cause a change of weight on ignition, water is estimated by igniting a weighed portion of the powdered silicate and noting the loss in weight. In the presence of ferrous iron and similar substances, it is determined by heating a known quantity of the pulverized material in a tube through which a current of dry air is drawn, the moisture expelled from the substance being collected in a weighed calcium chloride tube.

ESTIMATION OF THE ACID RADICAL IN ACETATES.

Solution.—All metallic acetates are soluble in water ; for that reason acetates cannot be estimated by direct gravimetric methods.

Estimation as Barium Sulphate, $BaSO_4$.—Free acetic acid is almost always estimated by volumetric analysis. But in the absence of other acids giving soluble barium salts, acetic acid may be determined by adding an excess of pure barium carbonate to the solution, filtering, and estimating the barium in the filtrate, as sulphate, by the directions given under the estimation of barium. Each molecular weight of barium sulphate indicates two acetic acid radicals.

The estimation of the acetic acid of acetates is usually accomplished as follows. A weighed quantity (about 1 gramme) of the sample is placed in a small distillation bulb or flask with a long neck, a little distilled water added, and then a solution of 5 grammes of glacial phosphoric acid in 10 c.c. of water. The flask is then heated to distil off the acetic acid, care being taken to prevent bumping. When the contents of the flask have become nearly dry, 25 c.c. of distilled water are added, and the distillation to a small bulk repeated. If three or four more such portions of water are added and distilled off in the same manner, all of the acetic acid will be found in the distillates. These are mixed and titrated with a standard alkali solution, phenolphtaleïn being used as indicator. From the number of c.c. of alkali solution required, and the value of this solution in acetic acid, the real acetic acid contained in the acetate is calculated.

ESTIMATION OF THE ACID RADICAL IN OXALATES.

Solution.—The oxalates of the alkali metals are soluble in water. The remaining oxalates require to be decomposed by alkali carbonates, ammonium sulphide, or hydrogen sulphide in order to bring the acid radical into solution as alkali oxalate for gravimetric estimation.

Estimation as Calcium Oxide, CaO.—The solution of the alkali oxalate is slightly acidified with acetic acid, and precipitated with calcium acetate solution. The mixture is set aside to allow the calcium oxalate to settle. The clear, supernatant liquid is then decanted to a filter, and the precipitate treated exactly as in the estimation of calcium as calcium oxide. Free oxalic acid is usually neutralized before the addition of the calcium salt. Each molecule of calcium oxide represents one molecule of oxalic acid or its radical.

ESTIMATION OF THE ACID RADICAL IN TARTRATES.

Solution.—The normal tartrates of the alkali metals are soluble in water, as is also sodium bitartrate; the bitartrates of potassium and ammonium are only sparingly soluble in water, but they may be converted into soluble normal tartrates by the addition of alkali hydrate or carbonate. Antimony and potassium tartrate, iron and potassium tartrate, and iron and ammonium tartrate are all soluble in water. The remaining tartrates are insoluble in water, but dissolve in hydrochloric or nitric acid; their acid radical, and that of the double tartrates just mentioned, is brought into solution as alkali tartrate by the methods given for the solution of oxalates. The following methods of estimation yield approximate results:

Estimation as Lead Tartrate, $PbC_4H_4O_6$.—For this estimation the solution must contain no other acid that precipitates with lead acetate. The neutral solution of the tartrate is mixed with an excess of lead acetate, the precipitate is collected on balanced filters, washed with diluted alcohol, dried at 100°, and weighed.

Estimation as Calcium Oxide, CaO.—The conditions for the application of this method are a neutral solution and the absence of other acids precipitable by calcium salts. In addition, the solution must be freed from any ammonium salts by warming it with a slight excess of fixed alkali hydrate; after the ammonia is expelled the solution is neutralized with acetic acid. Calcium chloride is used to precipitate the tartaric acid. The precipitate of calcium tartrate, $CaC_4H_4O_6$, is allowed to stand in the mixture for several hours, then collected, washed with diluted alcohol, dried, and ignited to a constant weight with a blast-lamp. The product of ignition is calcium oxide, which indicates tartaric acid, or its radical, molecule for molecule.

Estimation as Acid Potassium Tartrate, $KHC_4H_4O_6$.—This form may be used to estimate tartaric acid in the presence of acids which interfere with the preceding methods, as, for instance, citric, oxalic, sulphuric, phosphoric, and boric acids. Acid solutions are first neutralized with sodium hydrate. The solution should be concentrated. It is acidified with acetic acid, mixed with alcohol, and precipitated with a strong solution of potassium acetate. The precipitate of acid potassium tartrate is collected on balanced filters, washed with alcohol to remove salts, dried at 100°, and weighed.

ESTIMATION OF THE ACID RADICAL IN CITRATES.

Solution.—The alkali citrates are soluble in water, and so are the citrates of magnesium, bismuth, and ammonium, and iron and ammonium; plain ferric citrate is dissolved more readily by hot water than by cold. Calcium citrate is soluble in cold water, but nearly insoluble in hot water. The citric acid of bismuth citrate, and of insoluble citrates in general, may be brought into solution by decomposing these salts with ammonium sulphide or sodium carbonate, as is best suited to the case. The soluble citrates of bismuth and iron with ammonium are also treated in this manner. The excess of ammonium sulphide is expelled from the filtrate by evaporation; the excess of alkali carbonate is destroyed by neutralizing the filtrate with acetic acid.

Estimation as Barium Citrate, $Ba_3(C_6H_5O_7)_2$.—The solution of the citrate must be neutral to litmus paper, contain all of the citric acid in the form of alkali citrate, and be free from other acids which are precipitated by barium. It is mixed with a slight excess of neutral solution of barium acetate. To this mixture is added a volume of alcohol equal to twice that of the mixture. The precipitate of barium citrate is collected on balanced filters, washed with 63 per cent. (by volume) alcohol,* and dried at 130° till the weight is constant. The barium citrate is sometimes converted into barium sulphate, and the barium weighed in that form, as a check on the preceding method. This is done because the barium citrate is apt to retain water. The conversion is effected by burning the filter, adding the ash to the precipitate, moistening these with sulphuric acid, evaporating, and igniting until the excess of sulphuric acid is removed. One molecule of barium citrate yields three molecules of barium sulphate.

ESTIMATION OF WATER IN SALTS.

Many salts contain water in their molecules. This water occurs in two forms,—viz., water of crystallization, which can be expelled without altering the molecule of the salt proper; and water of hydration, which is present in hydrates, and whose expulsion changes the hydrates to oxides.

Both kinds of water are determined by drying, or gently igniting, a weighed portion of the salt, and noting the loss in weight. In these estimations regard must be had for the influence of heat on the salt, lest the latter be decomposed with loss of other volatile substances than water. For instance, crystallized ferrous sulphate, $FeSO_4.7H_2O$, when heated to 115°, loses six molecules of its water of crystallization; the seventh molecule, however, remains until the salt is heated to about 300°. But in case this temperature is much exceeded decomposition of the salt will take place with loss of sulphur trioxide; however, the desired end may be reached by heating a weighed quantity of the salt to 115°, when all but one molecule of water will be given off, leaving a residue of $FeSO_4.H_2O$. The loss should be six-sevenths of the total theoretical amount of water in the salt. The strongly combined water of crystallization is sometimes termed water of halhydration. The process is usually carried out by heating an air-bath to the desired temperature, and then introducing a watch-glass, or uncovered crucible, containing a weighed quantity of the powdered substance to be deprived of water. After maintaining the heat for an hour, remove the vessel, allow it to cool in a desiccator, and note the loss in weight. Then put the vessel in the air-bath again for half an hour, and at the end of that time weigh it again. If the weight is unaltered from the first weighing, the loss shows the amount of water given off at the temperature of the bath. It may be desirable to dry those salts which gradually part with their water at different degrees of heat at each of these points, and to note the loss at the several temperatures.

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* Rules for making an alcohol of any required lower percentage from an alcohol of any given higher percentage will be found on page 317.

In estimations of water which require great accuracy, the salt is heated in a dry tube, and the aqueous vapor drawn into a weighed calcium chloride tube by means of an aspirator. The increase in weight of the calcium chloride tube shows the amount of water yielded by the salt. Care must be taken, of course, to dry the air that is drawn into the tube during the heating of the salt. Where a substance is to be ignited to drive off its water, it is put in a crucible.

The following list of official substances shows the temperature at which the Pharmacopœia directs each of them to be dried for the estimation of its total water :

Citric Acid, $H_3C_6H_5O_7.H_2O$	135°
Gallic Acid, $HC_7H_5O_5.H_2O$	100°
Alum, $Al_2K_2(SO_4)_4.24H_2O$	200°
Aluminum Hydrate, $Al_2(OH)_6$ (water of hydration)	redness
Aluminum Sulphate, $Al_2(SO_4)_3 16H_2O$	200°
Antimony and Potassium Tartrate, $(K(SbO)C_4H_4O_6)_2.H_2O$	110°
Bismuth Subnitrate	120°
Caffeine, $C_8H_{10}N_4O_2.H_2O$	100°
Dried Calcium Sulphate	204°
Cinchonidine Sulphate, $(C_{19}H_{22}N_2O)_2H_2SO_4.3H_2O$	100°
Cinchonine Sulphate, $(C_{19}H_{22}N_2O)_2H_2SO_4.2H_2O$	100°
Codeine, $C_{18}H_{21}NO_3.H_2O$	100°
Copper Sulphate, $CuSO_4.5H_2O$ *	260°
Ferrous Sulphate, $FeSO_4.7H_2O$ (six molecules)	115°
Hyoscine Hydrobromate, $C_{17}H_{21}NO_4HBr.3H_2O$	100°
Magnesium Sulphate, $MgSO_4.7H_2O$	238°
Manganese Sulphate, $MnSO_4.4H_2O$	gentle ignition
Morphine, $C_{17}H_{19}NO_3.H_2O$	100°
Morphine Hydrochlorate, $C_{17}H_{19}NO_3.HCl.3H_2O$	100°
Morphine Sulphate, $(C_{17}H_{19}NO_3)_2H_2SO_4.5H_2O$	130°
Lead Acetate, $Pb(C_2H_3O_2)_2.3H_2O$	40°
Potassium Citrate, $K_3C_6H_5O_7.H_2O$	200°
Potassium Ferrocyanide, $K_4Fe(CN)_6.3H_2O$	100°
Quinidine Sulphate, $(C_{20}H_{24}N_2O_2)_2H_2SO_4.2H_2O$	120°
Quinine, $C_{20}H_{24}N_2O_2.3H_2O$	125°
Quinine Bisulphate, $C_{20}H_{24}N_2O_2H_2SO_4.7H_2O$	100°
Quinine Hydrobromate, $C_{20}H_{24}N_2O_2HBr.H_2O$	100°

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* Supplied.

Quinine Hydrochlorate, $C_{20}H_{24}N_2O_2HCl.2H_2O$	120°
Quinine Sulphate, $(C_{20}H_{24}N_2O_2)_2H_2SO_4.7H_2O$	115°
Quinine Valerianate, $C_{20}H_{24}N_2O_2C_5H_{10}O_2.H_2O$	100°
Sodium Acetate, $NaC_2H_3O_2.3H_2O$	123°
Sodium Arsenate, $Na_2HAsO_4.7H_2O$ *	148°
Sodium Borate, $Na_2B_4O_7.10H_2O$	red heat
Sodium Carbonate, $Na_2CO_3.10H_2O$ †	80°
Sodium Thiosulphate, $Na_2S_2O_3.5H_2O$	100°
Sodium Phosphate, $Na_2HPO_4.12H_2O$ *	100°
Sodium Pyrophosphate, $Na_4P_2O_7.10H_2O$	100°
Sodium Sulphate, $Na_2So_4.10H_2O$	100°
Sodium Sulphite, $Na_2SO_3.7H_2O$	100°
Sodium Sulphocarbolate, $NaSO_3C_6H_4(OH).2H_2O$	100°
Sparteine Sulphate, $C_{15}H_{26}N_2H_2SO_4.4H_2O$	100°
Strontium Lactate, $Sr(C_3H_5O_3)_2.3H_2O$	110°
Strychnine Sulphate, $(C_{21}H_{22}N_2O_2)_2H_2SO_4.5H_2O$	110°
Zinc Sulphate, $ZnSO_4.7H_2O$	110°

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* When sodium arsenate and phosphate are heated to redness, they lose water and are converted into pyroarsenate and pyrophosphate, according to the following reaction:

$$2Na_2HAsO_4 = Na_4As_2O_7 + H_2O.$$

† Supplied.

CHAPTER II.

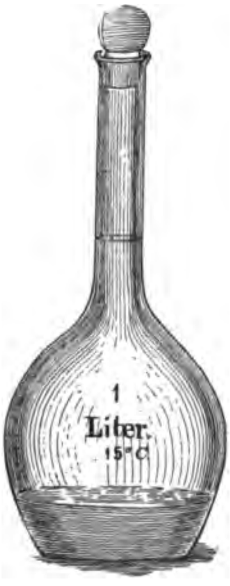
VOLUMETRIC PROCESSES.

SECTION I.

PRELIMINARY CONSIDERATIONS.

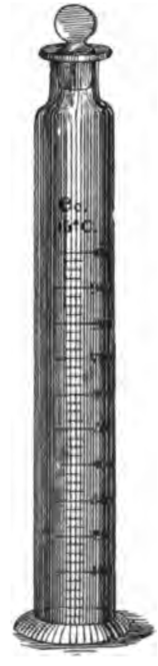
VOLUMETRIC analysis is the process of determining the amount of a substance by the use of a suitable reagent in a solution of known strength. These reagents in solution are known as *volumetric solutions*, and "are designated as normal ($\frac{N}{1}$) when they contain in 1 liter the molecular weight of the active reagent, expressed in grammes, and reduced to the valency corresponding to one atom of replaceable hydrogen or its equivalent."—U. S. P.

FIG. 8.



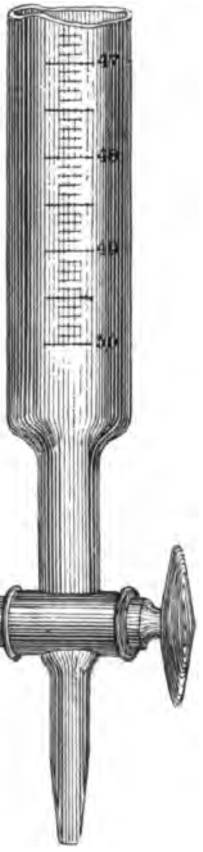
Liter flask.

FIG. 9.



Graduated cylinder.

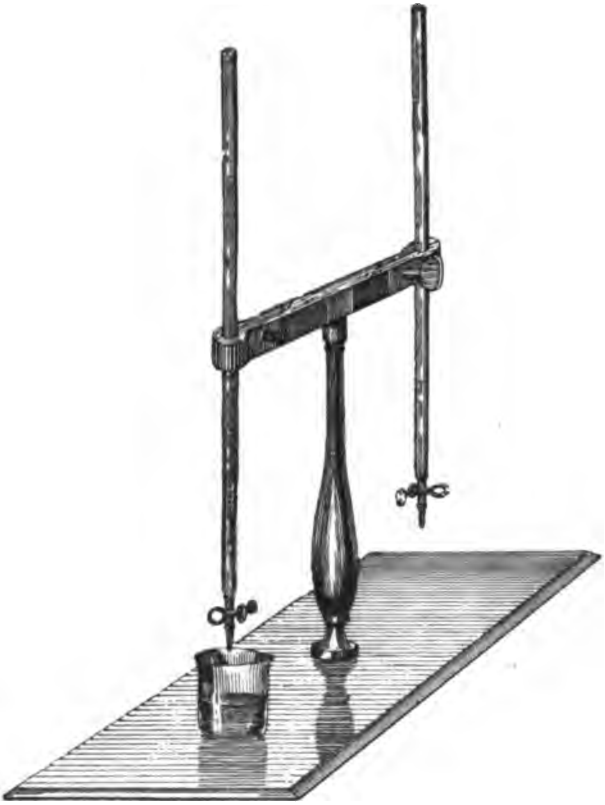
FIG. 10.



Geissler burette.

A decinormal solution ($\frac{N}{10}$) is one-tenth the strength of the normal one; and for many operations solutions of this strength are preferable. A centinormal solution ($\frac{N}{100}$) is one-hundredth the strength of the normal one. A standard solution is any volumetric solution whose strength is known. Solutions containing quantities in grammes of the active reagent having no simple relation to the number expressing its molecular weight are called empirical solutions. The term volumetric solution is sometimes designated by the abbreviation V. S. The abbreviation T. S. applies to test-solution.

FIG. 11.



Burettes and holder.

The apparatus required for volumetric operations consists of a *liter flask* (Fig. 8), a 1000 c.c. *cylinder*, graduated (Fig. 9), a 100 c.c. *cylinder*, graduated, 2 *burettes* of 50 or 100 c.c. capacity, graduated to $\frac{1}{10}$ c.c.,—the form known as Geissler's (Fig. 10) is the most desirable,—a suitable *holder* (Fig. 11) for these, and a few *pipettes*, assorted sizes, some of which are graduated to $\frac{1}{10}$ c.c.

Most volumetric apparatus is graduated to hold the number of cubic centimeters indicated,—at the temperature 15° C. or 15.5° C.; hence it is necessary not to deviate from the specified temperature in making volumetric solutions, or in using them in testing.

All measuring vessels employed for volumetric analysis should agree among themselves in accuracy of graduation.

Volumetric solutions are prepared in two ways. When the reagent is obtainable in a pure state, the exact amount of it is weighed and dissolved in sufficient solvent to make one liter. The preparation of oxalic acid volumetric solution is an example of this method. In the case of chemicals which cannot be obtained in an absolutely pure condition, a somewhat larger quantity of the sample than the weight of pure substance required in a liter of the volumetric solution is dissolved in enough liquid to make a liter; the strength of this solution is then found by causing it to react with an appropriate volumetric solution of known strength, and the volume of it that completely changes a liter of this volumetric solution is then diluted to one liter, in order to obtain in that volume the exact amount of reagent required. This method of preparing volumetric solutions is known as standardization; it is employed to adjust the strength of potassium hydrate volumetric solution (which see) and many other volumetric solutions. The manner in which the United States Pharmacopœia accomplishes the same end is illustrated in the preparation of normal sulphuric acid volumetric solution. When volumetric solutions are to be kept for some time they should be put into well-stoppered bottles and securely protected from light. All bottles in which volumetric solutions are to be kept, as well as the burettes or pipettes in which they are to be measured, should, prior to use, be rinsed with a small quantity of the solution they are to contain. The strength of solutions which have been kept should always be carefully determined before use by trial against a solution whose strength is known to be correct.

The substance which is to be estimated by volumetric analysis must always be dissolved before adding the volumetric solution. Water is the common solvent. The means of effecting the solution of substances which are insoluble in water are treated of under the description of the various volumetric solutions. When weighing out portions of a substance which is to be tested volumetrically, it will, in case of soluble substances, be advantageous to weigh out a quantity that will suffice for several repetitions of the test. The quantity so taken can be dissolved in a suitable volume of liquid, and an aliquot part of the solution taken for each of the several tests.

Volumetric analysis is accomplished by carefully dropping the volumetric solution from a burette into a solution of the substance to be estimated. In filling the burette with the volumetric solution care must be taken to completely fill the tube below the glass stop-cock or pinch-cock. If any difficulty is experienced in forcing the air out of this part when the instrument is provided with a rubber tube and pinch-cock, the operator will find it easy to overcome by pointing the end of the small tube that is inserted into the rubber tube upward and opening the pinch-cock. The solution of the substance to be estimated is contained in a flask or beaker, and should be constantly shaken or stirred during the addition of the volumetric solution. The process of adding the volumetric solution from a burette or other graduated apparatus is called titration. In another sense the term titration implies the estimation of a substance by volumetric analysis. Some well-defined chemical reaction takes place between the active reagent of the volumetric solution and the substance being estimated; the titration is continued until this reaction ceases. The terms *acidimetry* and *alkalimetry* are applied to the processes of estimating acids and alkalies respectively by neutralization, and, therefore, usually by the employment of volumetric solutions. Residual titration is a term used to signify that a quantity of volumetric solution known to be in excess is added and the excess determined by titrating back with a volumetric solution of opposite character. If the two solutions are of the same denomination, the number of c.c. of the first actually required in the estimation is found by deducting the volume of the second used from the volume of the first originally added.

To find the correct volume of a volumetric solution that has been used from a burette, the operator should bring his eye on a level with the surface of the liquid in the instrument and always read at the same part of the meniscus; that is to say, if he begins the titration with the bottom of the meniscus coinciding with the o or other graduation mark, he should take the reading on the burette at the bottom of the meniscus when the titration is finished. Either the top or bottom of the meniscus may be observed, provided it is used both at the beginning and end of the same titration. To indicate the completion of the chemical changes which occur in titrations reagents known as indicators are employed. These substances are intended to act with the slightest excess of the volumetric solution over and above that required to change the material to be estimated, and produce a visible effect, whereby it may be known that sufficient of the volumetric solution has been added.

The following list of indicators embraces those referred to in this book ; the directions for their preparation are taken from the United States Pharmacopœia, when given in that work :

Brazil-Wood Test-Solution.—Boil 50 gm. of finely cut Brazil-wood [the heart-wood of *Peltophorum dubium* (Sprengel) Britton, nat. ord. Leguminosæ] with 100 c.c. of water during half an hour, replacing the water from time to time. Allow the mixture to cool, strain, wash the contents of the strainer with water until 100 c.c. of strained liquid are obtained, add 25 c.c. of alcohol, and filter. This solution turns purplish-red with alkalies, and yellow with acids. Its chief employment is in the titration of the alkaloids of nux vomica.

Cochineal Test-Solution.—Macerate 1 gm. of unbroken cochineal [Coccus, U. S. P.], during four days, with 20 c.c. of alcohol and 60 c.c. of water. Then filter. The color of this test-solution turns violet with alkalies, and yellowish-red with acids. Its chief use is in the estimation of ammonia or alkaline earths.

Eosin Test-Solution.—Dissolve 1 gm. of commercial "yellowish" eosin [$K_2C_{20}H_6Br_4O_5$] in 30 c.c. of water. This solution is red by transmitted light, and shows a strong green fluorescence by reflected light. Acids destroy the fluorescence, and alkalies restore it. This indicator is used in the titration of the acidity of wine.

Ferric Ammonium Sulphate Test-Solution.—Dissolve 10 gm. of ferric ammonium sulphate [Ferri et Ammonii Sulphas, U. S. P.] in enough water to make 100 c.c. This indicator is used in connection with potassium sulphocyanate volumetric solution, with a slight excess of which it produces a reddish-brown tint.

Fluorescein Test-Solution.—Agitate 1 gm. of fluorescein [$C_{20}H_{12}O_5$] with 100 c.c. of diluted alcohol, until the latter is saturated ; then filter. This solution shows a strong green fluorescence, by reflected light, in the presence of the least excess of an alkali. It is used as an indicator in the estimation of the acidity of red wine.

Hæmatoxylin Test-Solution.—This is prepared by dissolving 1 gm. of pure crystallized hæmatoxylin in 100 c.c. of alcohol. The solution imparts a violet-red color to alkaline solutions and a pale-yellow color to acid solutions. This indicator is employed in the volumetric estimation of alkaloids by titration with standard acids.

Lacmoid Test-Solution.—2 gm. of lacmoid are dissolved in 1 liter of diluted alcohol. The color of the solution is turned red by acids, and the blue color restored by alkali. The color is affected by carbon dioxide. Alkali and alkaline-earth hydrates and mineral acids may be titrated in the cold by the use of this indicator. When used in the titration of carbonates and bicarbonates of the alkali and alkaline-earth metals, the solutions must be boiled to cause the expulsion of carbon dioxide, which affects the color of the indicator like an acid.

Litmus Test-Solution.—Exhaust coarsely powdered litmus with boiling alcohol (which removes a peculiar, red coloring matter, erythrolitmin), and digest the residue with about an equal weight of cold water, so as to dissolve the excess of alkali present. Finally extract the residue with about 5 times its weight of boiling water, and filter. Preserve the filtrate, as test-solution, in wide-mouthed bottles stoppered with loose plugs of cotton to exclude dust but to admit air. Acids in general change the blue color of litmus to red; alkalies restore the blue color. Carbon dioxide gives a wine-red color with litmus. On that account solutions of carbonates must be boiled to expel this gas as it is liberated by the volumetric acid solution. Boric acid gives a similar color.

Methyl-Orange Test-Solution.—Dissolve 1 gm. of methyl-orange [the sodium or ammonium salt of dimethylamidoazobenzolsulphonic acid, $HC_{14}H_{14}N_3SO_3 = 304.47$; also known as helianthin, or tropæolin D, or Poirrier's Orange 3 P] in 1000 c.c. of water. Add to it, carefully, diluted sulphuric acid, in drops, until the liquid turns red and just ceases to be transparent. Then filter. The solution acquires a yellow color when brought in contact with alkali hydrates, carbonates, or bicarbonates. Carbonic acid does not affect it, but sulphuric, hydrochloric, and other acids change its color to crimson. It is not suited for use with organic acids.

Phenolphtalein Test-Solution.—Dissolve 1 gm. of phenolphtalein [$C_{20}H_{14}O_4$] in 100 c.c. of diluted alcohol. The solution is colored deep purplish-red by alkali hydrates or carbonates; bicarbonates and most other salts do not produce such color; acids render the reddened solution colorless. It is not suitable as an indicator for ammonia. It can be used in the titration of carbonates and bicarbonates, if the solutions are boiled after the red color is discharged by the acid volumetric solution; should the red color appear, it is to be again discharged and the boiling repeated,—the two treatments being alternately made until the red color fails to reappear after several minutes' boiling. When used with phosphoric acid several times the ordinary quantity of the test-solution is needed.

Potassium Chromate Test-Solution.—Dissolve 1 gm. of potassium chromate, $K_2CrO_4 = 193.9$, in enough water to make 10 c.c. On adding silver nitrate T. S. to a little of the solution, a red precipitate is produced which should be completely dissolved by nitric acid (absence of chloride). Another portion of the solution, mixed with an equal volume of diluted hydrochloric acid, should yield no precipitate with barium chloride T. S. (absence of sulphate). This solution is used as an indicator for silver nitrate volumetric solution, the excess of the latter causing the formation of red silver chromate.

Potassium Dichromate Test-Solution.—Dissolve 10 gm. of potassium dichromate [Potassii Bichromas, U. S. P.] in enough water to make 100 c.c. This solution is used with silver nitrate volumetric solution, in place of potassium chromate test-solution; its advantage over the latter is that it does not form insoluble compounds with the haloid salts of barium and strontium, during their titration with silver nitrate volumetric solution.

Potassium Ferricyanide Test-Solution.—Dissolve 1 part of potassium ferricyanide, $K_6Fe_2(CN)_{12} = 657.7$, in about 10 parts of water. This solution should be made freshly when required, as it is rapidly decomposed by light. A freshly prepared, aqueous solution, when mixed with some ferric chloride T. S. and diluted with water, should show a brown tint, free from turbidity or a shade of green. The solution is used as an indicator for potassium dichromate volumetric solution, to show when all of a ferrous salt has been oxidized to the ferric condition. It produces a blue precipitate with soluble ferrous salts, but only a reddish-brown color with ferric salts.

Potassium Ferrocyanide Test-Solution.—Dissolve 10 gm. of potassium ferrocyanide, $K_4Fe(CN)_6.3H_2O = 421.76$, in enough water to make 100 c.c. This solution is sometimes used in connection with alkaline cupric tartrate volumetric solution, to show when all of the copper has been precipitated from solution or reduced to the cuprous state.

Rosolic Acid Test-Solution.—Dissolve 1 gm. of commercial rosolic acid [chiefly methyl-aurin, $C_{20}H_{16}O_3 = 303.28$] in 10 c.c. of diluted alcohol, and add enough water to make 100 c.c. The solution turns violet-red with alkalies, yellow with acids. In place of rosolic acid, commercial pæonin (also known as aurin R) [chiefly $C_{19}H_{14}O_3 = 289.31$] may be employed. This indicator is especially adapted for use in the titration of ammonium compounds.

Starch Test-Solution.—Mix 1 gm. of starch with 10 c.c. of cold water, and then add enough boiling water, under constant stirring, to make about 200 c.c. of a thin, transparent jelly. If it is desired to preserve this test-solution for any length of time, 10 gm. of zinc chloride, $ZnCl_2 = 135.84$ [Zinci Chloridum, U. S. P.], should be added to it, and the solution transferred to small bottles, which should be well stoppered. Starch test-solution is used to indicate the presence of free iodine, with which it gives a blue color. This solution is used with iodine volumetric solution, also with sodium hyposulphite volumetric solution, which destroys the blue color in question. Heat also destroys the blue color; hence the solution to be titrated must always be cold.

Indicators intended for acidimetry and alkalimetry should be examined as to their neutrality before being used. If necessary, they should be brought, by the cautious addition of diluted sulphuric acid, or of a dilute solution of an alkali, to such a point that, when a few drops of one of them are added to 25 c.c. of water, a single drop of a centinormal acid or alkali V. S., respectively, will distinctly develop the corresponding tints. The required degree of purity of other indicators should also be established before they are employed. Since many of the colored test-solutions are injured by exposure to light, it is best to preserve them in dark amber-colored vials.

In most cases a few drops of the indicator are mixed with the solution to be titrated, and the volumetric solution then run in until the reaction is at an end. In a few instances the indicator is not applied in this manner, but after each addition of the volumetric solution a little of the liquid is taken from the beaker and tested with a drop of the indicator until the change is found to be complete.

The terms *standard* and *titer* are used to designate the strength of a volumetric solution in active reagent per cubic centimeter or liter. The derivation of the strengths of each solution is explained in the discussion of the respective case.

The quantity of any particular substance that is indicated by the use of 1 c.c. of a volumetric solution is known as the equivalent, value, factor, or coefficient of the volumetric solution for that substance. These quantities are derived from the amounts of the different substances that react with the active reagent of the volumetric solution. For example, if we represent the reaction between calcium hydrate and oxalic acid which takes place in the official assay of lime water, and indicate the molecular quantities that take part therein, we find it expressed by the following equation and numbers:

$$\underset{73.83}{Ca(OH)_2} + \underset{125.70}{H_2C_2O_4.2H_2O} = CaC_2O_4 + 4H_2O.$$

If these molecular quantities be now converted into actual weights, we will see that 73.83 grammes of calcium hydrate are required to produce a complete reaction with 125.70 grammes of oxalic acid. But in a liter of normal oxalic acid volumetric solution we have only 62.85 grammes, or one-half the preceding amount of oxalic acid; therefore 1 liter of normal oxalic acid volumetric solution will react with only 36.915 grammes of calcium hydrate. A liter of decinormal oxalic acid volumetric solution contains but 6.285 grammes of oxalic acid, and, on that account, will react with but 3.6915 grammes of calcium hydrate. One c.c. is the one-thousandth part of a liter; hence 1 c.c. of decinormal oxalic acid volumetric solution will contain 0.006285 gramme of oxalic acid, and its use will indicate 0.003691 gramme of calcium hydrate.

The usual method of calculating the result of a volumetric analysis consists in multiplying the value of 1 c.c. of the volumetric solution in the substance being estimated by the number of c.c. of the volumetric solution used in the titration to find the total amount of the absolute substance present, and then making a proportion in the usual way to calculate the percentage amount of the absolute substance present in the article tested.

The calculation of the result at the end of the analysis may be reduced to a simple multiplication by taking of the substance to be analyzed a weight equivalent to the weight of the constituent to be determined which corresponds to 100 c.c. of the volumetric solution to be used. By so doing, each c.c. of the volumetric solution required in the titration indicates 1 per cent. of the constituent being determined. The United States Pharmacopœia makes frequent use of this method of calculating results; illustrations of the same will be found in the cases of the official assays of chlorinated lime given on page 166, and of syrup of ferrous iodide on page 187. The Pharmacopœia also uses various modifications of this method, as, for instance, half the quantity or twice the quantity required by the foregoing specification is directed to be taken for analysis, and the number of c.c. of volumetric solution employed accordingly multiplied or divided by two to find the percentage of the constituent. It is self-evident that, for these methods of calculation to be valid, the material to be estimated must not in any case contain more than one constituent capable of reacting with the volumetric solution.

A preliminary qualitative analysis should therefore always be made to inform the operator on this point. When two such substances are present, another form of calculation, which takes into account their relative effects, is employed, and by it the amount of each substance may be determined. An illustration of the method of calculation resorted to in a case like the foregoing is given on page 184, in the estimation of potassium bromide. Guided by the principles involved in this method, the Pharmacopœia in the last-named and some other cases specifies a certain quantity of the substance to be taken, and exacts this amount to require a stated volume of the volumetric solution in order to indicate the official strength or degree of purity of the substance.

SECTION II.

THE PREPARATION AND USES OF VOLUMETRIC SOLUTIONS.

Decinormal Oxalic Acid Volumetric Solution.

Containing 6.285 grammes of $H_2C_2O_4.2H_2O$ *in 1 liter.*

The preparation of this solution is usually the starting point in the operations involving the estimation of acids and alkalies. Oxalic acid may be purchased in a pure state or can be purified by making a saturated solution of the acid in water, filtering, and concentrating to three-fourths of its volume. The first crop of crystals which separates from the liquid upon cooling is rejected as containing salts; by further evaporation of the mother liquor a second crop is obtained. These are drained, thoroughly dried by pressing between sheets of filter paper, and preserved as pure. 6.285 grammes of the pure acid are weighed, transferred to a liter flask, about 500 c.c. of distilled water are added, and the crystals dissolved. The whole is brought to a temperature of about 15°, and with distilled water of the same temperature the solution is diluted to the volume of 1 liter.

Oxalic acid volumetric solution is used for the estimation of alkalies and potassium permanganate; it acts by neutralizing the former and by reducing the latter. As oxalic acid [$H_2C_2O_4.2H_2O$ = 125.70] is a dibasic acid, it is necessary for the normal volumetric solution to contain but one-half the molecular weight of oxalic acid, expressed in grammes, in order to have its strength correspond to one atom of replaceable hydrogen. This solution may also be used for the estimation of the organic salts of the alkalies and alkaline earths (after their conversion into carbonates by ignition) and for the estimation of soluble lead salts, as described under the consideration of normal sulphuric acid volumetric solution. It is also employed in the standardization of volumetric alkali solutions.

One cubic centimeter of decinormal oxalic acid volumetric solution is equivalent to the following:

	Gramme.
Oxalic Acid, crystallized, $H_2C_2O_4.2H_2O$	0.006285
Ammonia Gas, NH_3	0.001701
Calcium Hydrate, $Ca(OH)_2$	0.003691
Potassium Hydrate, KOH	0.005599
Potassium Permanganate, $K_2Mn_2O_8$	0.0031534
Sodium Hydrate, NaOH	0.003996

Estimation of Potassium Hydrate.

One of the simplest estimations with the volumetric solution of oxalic acid is that of potassium hydrate. From 2.500 to 3 grammes of the hydrate are weighed in a closely corked, clean, dry test-tube, rinsed out into a graduated cylinder, and dissolved in enough water to make 100 c.c. The resulting solution is put into a burette; then 20 c.c. (one-fifth) of it are drawn from this instrument into a beaker and colored with a few drops of phenolphtalein solution. The beaker, with its contents, is set under a burette containing some of the oxalic acid solution. This solution is slowly run in, and the mixture constantly stirred with a glass rod until the red color just ceases to be visible. The proof of this is that one drop of a similar alkali solution will restore the red color.

The following equation expresses the reaction between the alkali hydrate and the oxalic acid of the volumetric solution :

$$2KOH + H_2C_2O_4.2H_2O = K_2C_2O_4 + 4H_2O.$$

If 0.500 gramme of potassium hydrate were contained in the aliquot part of the alkali solution used, and it were pure, it would be found that 89.3 c.c. of the oxalic solution had been used ; but if we suppose that 85 c.c. were necessary, then, as every cubic centimeter of the oxalic acid solution is equal to 0.005599 gramme of potassium hydrate, we have 85 × 0.005599 = 0.476, the amount of potassium hydrate found. The following proportion will then yield the percentage of absolute potassium hydrate in the sample :

0.500 : 476 :: 100 : 95.20 per cent.

The estimation of sodium hydrate is conducted in the same way as that of potassium hydrate. In weighing ammonium hydrate, a stoppered flask or bottle should be used, and care taken to prevent the liquid from coming in contact with the cork and thus being lost. Rosolic acid is used as indicator in the titration of ammonium compounds.

For the estimation of lime water, the principal form of calcium hydrate, a measured volume of the solution is taken from a burette and titrated with oxalic acid volumetric solution, phenolphtalein being used as indicator. The number of c.c. of lime water used are taken, in the calculation of the result, as weighing so many grammes.

The estimation of potassium permanganate is performed by dissolving a weighed quantity of the compound in boiling distilled water, cautiously adding some strong sulphuric acid to the solution so obtained, and titrating with oxalic acid volumetric solution until complete decoloration of the permanganate solution is effected. The reaction is as follows :

$$K_2Mn_2O_8 + 5H_2C_2O_42H_2O + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 18H_2O.$$

Decinormal Potassium Hydrate Volumetric Solution.

Containing 5.599 grammes of KOH *in 1 liter.*

As potassium hydrate is not obtainable, except it contains an unknown amount of water, it is necessary to standardize its solution. For this purpose about 7.5 grammes of the hydrate are taken, transferred to a graduated cylinder, and 1000 c.c. of distilled water added. 50 c.c. of decinormal solution of oxalic acid are placed in a beaker, a few drops of phenolphtalein solution added, and the alkaline solution added from a burette until the red color of the indicator just begins to appear.

If it has required 45 c.c. of the potassium hydrate solution to neutralize 50 c.c. of the oxalic acid solution, then it is evident that 900 c.c. of the former, when diluted to 1000, would have the same strength as the oxalic acid volumetric solution ; in other words, the one would neutralize the other volume for volume. After the dilution in this manner, a new trial should be made to prove that the correspondence of the solutions is perfect.

Potassium hydrate volumetric solution is used for the estimation of most free acids and acid salts, all of which, except phosphoric acid, it converts in the process into neutral salts, water being formed at the same time. As the potassium hydrate acts by replacing the hydrogen of the acids with potassium to form neutral potassium salts, and as the hydrate contains but one atom of the metal, and as it is univalent, the whole molecular weight in grammes of the potassium hydrate is taken for 1 liter of normal solution. The normal solution is the strength usually employed.

The estimation of the acids and acid salts is conducted by weighing out a convenient portion of the sample, dissolving it in water or diluting it with this liquid, placing the solution in a beaker, and running in the potassium hydrate solution until neutralization is effected. In weighing the fluid acids, a stoppered flask or bottle should be used, and care taken to prevent the liquid from coming in contact with the cork and thus being lost.

Phenolphtalein is generally used as indicator in these estimations, the alkali solution being added until a permanent red color is established in the solution in the beaker.

One cubic centimeter of decinormal potassium hydrate volumetric solution is equivalent to the following :

	Gramme.
Potassium Hydrate, KOH	0.005599
Sodium Hydrate, $NaOH$	0.003996
Ammonia Gas, NH_3	0.001701
Ammonium Chloride, NH_4Cl	0.005338
Acetic Acid, absolute, $HC_2H_3O_2$	0.005986
Citric Acid, crystallized, $H_3C_6H_5O_7H_2O$	0.006983
Hydrobromic Acid, absolute, HBr	0.008076
Hydrochloric Acid, absolute, HCl	0.003637
Hydriodic Acid, absolute, HI	0.012753
Hypophosphorous Acid, HPH_2O_2	0.006588
Lactic Acid, absolute, $HC_3H_5O_3$	0.008979
Nitric Acid, absolute, HNO_3	0.006289
Oxalic Acid, crystallized, $H_2C_2O_4.2H_2O$	0.006285
Phosphoric Acid, H_3PO_4 (to form K_2HPO_4; with phenol-phtaleïn)	0.004890
Phosphoric Acid, H_3PO_4 (to form KH_2PO_4; with methyl-orange)	0.009780
Potassium Dichromate, $K_2Cr_2O_7$	0.014689
Sulphuric Acid absolute, H_2SO_4	0.004891
Tartaric Acid, crystallized, $H_2C_4H_4O_6$	0.007482

When phenolphtalein is used in the titration of phosphoric acid, twice the volume of potassium hydrate solution is required to cause the appearance of the color of the indicator as when methyl-orange is employed for the same purpose. The reactions in the case of phosphoric acid are—with phenolphtalein as indicator—

$$H_3PO_4 + 2KOH = K_2HPO_4 + 2H_2O,$$

and with methyl-orange as indicator—

$$H_3PO_4 + KOH = KH_2PO_4 + H_2O.$$

Potassium hydrate volumetric solution converts potassium dichromate into neutral potassium chromate according to the following reaction :

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + 2H_2O.$$

Phenolphtalein is employed in this titration. In the estimation of the sulphuric acid contained in the official aromatic sulphuric acid, a weighed portion of the latter is put in a flask and diluted with five times its bulk of water ; this mixture is boiled for 10 minutes, then allowed to cool, mixed with a few drops of phenolphtalein solution, and titrated with potassium hydrate solution until it acquires a permanent pink tint.

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Centinormal potassium hydrate volumetric solution is used in the assay of extract of nux vomica, and other preparations of this drug, to neutralize the excess of decinormal sulphuric acid employed. Brazil-wood test-solution is used as indicator in this case. (See page 225.)

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Decinormal Sodium Hydrate Volumetric Solution.

Containing 3.996 grammes of $NaOH$ *in 1 liter.*

5.4 grammes of sodium hydrate are dissolved in 1000 c.c. of water, and the solution standardized, as in the case of potassium hydrate volumetric solution, by titration against decinormal oxalic acid volumetric solution, phenolphtalein being used as indicator. The action of this solution is the same as that of potassium hydrate V. S. The full molecular weight in grammes of the reagent is taken for 1 liter of the normal solution because sodium hydrate is a monacid base. The same indicators are used. The table of equivalents given for 1 c.c. of decinormal potassium hydrate volumetric solution applies also to this solution. Therefore decinormal sodium hydrate V. S. may be employed in place of decinormal potassium hydrate V. S., volume for volume. The latter, however, is preferable, since it foams less, and attacks glass more slowly and less energetically.

Decinormal Barium Hydrate Volumetric Solution.

Containing 8.541 grammes of $Ba(OH)_2$ *in 1 liter.*

To obtain this solution about 10 grammes of a sample of barium hydrate which has been protected from the carbon dioxide of the air is shaken with about 250 c.c. of water, and the solution so obtained filtered to remove any insoluble barium compounds. The clear liquid is diluted to about 1 liter and standardized against a decinormal acid volumetric solution, according to the directions given for the standardization of potassium hydrate solution, the strength of the barium hydrate solution being finally adjusted so that equal volumes of the latter and the acid exactly neutralize each other.

Decinormal barium hydrate volumetric solution is used for the estimation of the carbon dioxide in water, which it neutralizes; being a diacid base, one-half of the number which expresses the molecular weight of the substance is taken in grammes of barium hydrate for a liter of the normal solution, or one-tenth this quantity for a liter of decinormal solution.

The neutralizing strength of this solution is the same as that of decinormal potassium hydrate volumetric solution.

Phenolphtalein is generally used as indicator with this solution.

Normal Sodium Carbonate Volumetric Solution.

Containing 52.925 grammes of Na_2CO_3 *in 1 liter.*

This solution is sometimes used as the standard alkali solution for the estimation of acids, especially in the preparation of volumetric acid solutions, which are conveniently standardized by titration against it. It is also employed for the estimation of barium, strontium, and calcium in their soluble salts. It is prepared by dissolving 52.925 grammes of pure anhydrous sodium carbonate in enough distilled water to make 1 liter of solution. The pure anhydrous sodium carbonate is prepared by heating about 85 grammes of pure sodium bicarbonate,* with occasional stirring in a platinum crucible, to dull redness for ten minutes. The change which occurs during this treatment consists in a loss of water and carbon dioxide as follows:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

The crucible is allowed to cool in a desiccator; it is then placed on the balance and the slight excess of sodium carbonate over 52.925 grammes removed. The salt is then dissolved in the crucible by means of hot distilled water, the solution transferred to a liter flask, the crucible rinsed with several successive portions of water, the rinsings poured into the flask, and the contents of the latter made up to the liter mark by the addition of distilled water. The solution acts by neutralizing acids or by forming insoluble carbonates, and, since the salt contains two univalent sodium atoms available for the former purpose, and one bivalent carbonic acid residue capable of forming insoluble carbonates, half the molecular weight of the anhydrous salt in grammes of the substance are taken for 1 liter of solution.

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* Sodium bicarbonate is liable to contain as impurities chiefly traces of sodium chloride and sodium sulphate. The absence of these salts must be established before the salt can be used for preparing pure anhydrous sodium carbonate. Therefore a nearly saturated solution of the salt should be prepared, and separate portions of it acidified with nitric acid and tested with silver nitrate and barium chloride; in addition, it should be noted whether the solution is perfectly clear and free from settled or floating particles. If no impurities whatever are found, the salt may be converted at once into anhydrous sodium carbonate. But if either chlorides or sulphates are found, the bicarbonate must be previously freed from them by packing about half a pound of the salt in a funnel whose neck is stoppered by a plug of cotton, and pouring cold distilled water over it until the appropriate tests show the impurities to have been removed. If the original sample of the bicarbonate is found to contain insoluble matter, the substance is purified by making a saturated solution of the salt in boiling distilled water, filtering through paper while hot to remove insoluble matter, and allowing the clear filtrate to cool. The filtered liquid, which contains sodium carbonate and not bicarbonate, is constantly stirred while cooling, in order to make the salt separate in a granular condition; by producing this form, the sodium carbonate is obtained pure, the sodium chloride and sulphate remaining in the mother liquor.

In neutralizing power the solution is in every respect equal to normal potassium hydrate volumetric solution. When this solution is employed for the estimation of barium, strontium, and calcium in their soluble salts, the process is conducted as follows: a weighed portion of the salt is dissolved in water, the solution neutralized, if necessary, with sodium or potassium hydrate, a few drops of phenolphtalein solution added, the mixture heated to boiling, and the volumetric solution of sodium carbonate added from a burette, with occasional boiling, until a permanent red color is imparted to the contents of the vessel. The insoluble carbonates have no effect on the phenolphtalein; the red color appears only when the soluble sodium carbonate is no longer decomposed. Magnesium salts cannot be estimated in this manner, since the precipitate which they yield with sodium carbonate dissolves sparingly in water to give a feebly alkaline solution, and on that account disadvantageously affects the indicator.

A fiftieth normal solution is used for determining the hardness of water. (See page 299.) It is best prepared by dissolving 1.0588 grammes of pure sodium carbonate in enough water to make 1 liter.

Normal Sulphuric Acid Volumetric Solution.

Containing 48.91 grammes of H_2SO_4 *in 1 liter.*

About 30 c.c. of pure, concentrated sulphuric acid are carefully mixed with 1000 c.c. of water, and the mixture allowed to cool. 50 c.c. of the cool liquid are placed in a beaker, a few drops of phenolphtalein solution are added, and sufficient normal potassium hydrate volumetric solution is run in to just make the red color of the indicator appear. If 60 c.c. of the alkali solution have been necessary, then each 50 c.c. of the acid solution must be diluted to 60 c.c., or each 1000 c.c. to 1200 c.c. Another trial should be made with the diluted solution to prove that it is exactly the strength of the potassium hydrate solution, volume for volume.

Normal sulphuric acid volumetric solution is used to estimate alkalies, soluble lead salts, organic salts of the alkali metals and alkaline-earth metals, and carbonates of the alkaline earths. In the case of alkalies, it acts upon the borates, carbonates, and hydrates, converting them into neutral sulphates; in the second case it forms insoluble lead sulphate; in the third case it is employed to neutralize the carbonates that are left upon ignition of the organic salts of the metals named; its action in the fourth case is the same as in the third.

Normal sulphuric acid volumetric solution is exactly equal in neutralizing power to normal oxalic acid volumetric solution; it is preferred to the latter, which has a tendency to crystallize at the point of the burette. Hydrochloric acid volumetric solution is preferred to sulphuric acid volumetric solution for the titration of the hydrates and carbonates of the alkaline-earth metals, since it produces soluble compounds therewith. As sulphuric acid is a dibasic acid, like oxalic acid, one-half of the number which represents the molecular weight of the acid is taken in grammes of absolute sulphuric acid to make 1 liter of normal volumetric solution.

One c.c. of normal sulphuric acid volumetric solution is the equivalent of:

	Gramme.
Sulphuric Acid, absolute, H_2SO_4	0.04891
Ammonia Gas, NH_3	0.01701
Ammonium Carbonate, $(NH_4)_2CO_3$	0.042935
Ammonium Carbonate [U. S. P.], $NH_4HCO_3.NH_4NH_2CO_2$	0.05226
Calcium Carbonate, $CaCO_3$	0.04988
Lead Acetate, crystallized, $Pb(C_2H_3O_2)_2.3H_2O$	0.18900
Lead Subacetate, assumed as $Pb_2O(C_2H_3O_2)_2$	0.13662
Lithium Benzoate, $LiC_7H_5O_2$ (to be ignited)	0.12772
Lithium Carbonate, Li_2CO_3	0.036935
Lithium Citrate, $Li_3C_6H_5O_7$ (to be ignited)	0.0698566
Lithium Salicylate, $LiC_7H_5O_3$ (to be ignited)	0.14368
Potassium Acetate, $KC_2H_3O_2$ (to be ignited)	0.09789
Potassium Bicarbonate, $KHCO_3$	0.09988
Potassium Bitartrate, $KHC_4H_4O_6$ (to be ignited)	0.18767
Potassium Carbonate, anhydrous, K_2CO_3	0.068955
Potassium Citrate, crystallized, $K_3C_6H_5O_7.H_2O$ (to be ignited)	0.10786
Potassium Hydrate, KOH	0.05599
Potassium and Sodium Tartrate, $KNaC_4H_4O_6.4H_2O$ (to be ignited)	0.14075

	Gramme.
Sodium Acetate, $NaC_2H_3O_2.3H_2O$ (to be ignited)	0.13574
Sodium Benzoate, $NaC_7H_5O_2$ (to be ignited)	0.14371
Sodium Bicarbonate, $NaHCO_3$	0.08385
Sodium Borate, crystallized, $Na_2B_4O_7.10H_2O$	0.19046
Sodium Carbonate, anhydrous, Na_2CO_3	0.052925
Sodium Carbonate, crystallized, $Na_2CO_3.10H_2O$	0.142725
Sodium Hydrate, NaOH	0.03996
Strontium Lactate, $Sr(C_3H_5O_3)_2$ (to be ignited)	0.13244

Rosolic acid is used as indicator in the titration of ammonium compounds. Phenolphtalein is employed to indicate the end reaction in the estimation of potassium and sodium hydrates. Methyl-orange is used in the titration of carbonates. Its advantage is that carbonic acid does not affect it; it may be replaced by phenolphtalein, however, if the solution to be titrated is boiled, as described on page 147. In the estimation of lead in soluble lead salts, the volumetric solution of sulphuric acid is added in drops from the burette until a precipitate ceases to form. This result is attained by allowing the precipitate to subside after each addition of a small quantity of the volumetric solution. Sodium borate is estimated by dissolving it in a small quantity of water, adding a few drops of litmus test-solution, and titrating with normal sulphuric acid volumetric solution until the solution becomes bright red in color. The wine-red color which the litmus develops with the boric acid at the start is disregarded.

The organic salts of lithium, potassium, sodium, and strontium are ignited in a crucible or dish until nearly all of the carbon is consumed. The vessel is then allowed to cool, the residue is treated with some water, and titrated with normal sulphuric acid volumetric solution, methyl-orange being used as indicator. The change which takes place upon the ignition of these organic salts may be illustrated by the following behavior of potassium bitartrate under the influence of heat:

$$2KHC_4H_4O_6 + 5O_2 = K_2CO_3 + 7CO_2 + 5H_2O.$$

The sulphuric acid decomposes the potassium or other carbonate as follows:

$$K_2CO_3 + H_2SO_4 = K_2SO_4 + CO_2 + H_2O.$$

If satisfactory methyl-orange is not at hand, a volume of normal sulphuric acid solution, known to be an excess, may be added, the liquid boiled to expel carbon dioxide, and the excess of the acid solution determined by titrating back with standard potassium hydrate solution, using phenolphtalein as indicator.

Decinormal Sulphuric Acid Volumetric Solution.

Containing 4.891 grammes of H_2SO_4 *in 1 liter.*

Dilute 100 c.c. of normal sulphuric acid volumetric solution with enough water to make 1000 c.c.

Decinormal sulphuric acid is preferable in many cases to oxalic acid solution of the same strength, and is equivalent to the same quantities of the substances given under the latter.

It acts in the same manner as the normal sulphuric acid solution, and may be employed in the titration of the same substances as the latter; in the event of such use of it, however, the equivalents given in the table for each c.c. of the normal solution must be divided by ten. Its chief use is in the estimation of the combined alkaloids of nux vomica as described on page 224. Brazil-wood test-solution is used as indicator with it for that purpose.

One c.c. of decinormal sulphuric acid volumetric solution contains 0.004891 gramme of H_2SO_4, and is the equivalent of:

	Gramme.
Potassium Hydrate, KOH	0.005599
Combined alkaloids of Nux Vomica, assumed to consist of equal parts of Strychnine and Brucine	0.0364

gm.
36.46 = N

Fiftieth normal sulphuric acid volumetric solution is used in determining the hardness of water. (See page 299.) It may be prepared by diluting the decinormal solution with four times its volume of water.

Decinormal Hydrochloric Acid Volumetric Solution.

Containing 3.637 grammes of HCl *in 1 liter.*

13 c.c. of hydrochloric acid of specific gravity 1.163 are mixed with enough water to measure 1000 c.c. This solution is standardized against decinormal potassium hydrate volumetric solution. Hydrochloric acid being a monobasic acid, its normal solution is made to contain the entire molecular weight of the substance in grammes of absolute hydrochloric acid.

Decinormal hydrochloric acid volumetric solution is equivalent in neutralizing power to decinormal sulphuric acid, and may be employed, if more convenient, for the same purposes.

It is better adapted to the titration of alkaline-earth hydrates and carbonates than either volumetric solution of oxalic acid or sulphuric acid, as it forms soluble salts with the metals present.

The estimation of the hydrates may be done by direct titration, but in the case of carbonates it is better to add an excess of the volumetric acid solution and then determine the exact amount of it that is neutralized by titrating back with standard potassium hydrate solution.

This solution is sometimes used in the volumetric estimation of alkaloids. In such cases hæmatoxylin is usually used as indicator.

Decinormal Iodine Volumetric Solution.

Containing 12.653 grammes of Iodine in 1 liter.

12.653 grammes of pure iodine* are weighed out in a stoppered Erlenmeyer flask. 18 grammes of pure potassium iodide are also weighed on a watch-glass or in a beaker and transferred to the Erlenmeyer flask. A small quantity of cold water is then put into the flask, the latter closed with the stopper, and shaken by giving it a gyratory motion. Care must be taken to prevent loss through the liquid splashing upon the cork. When the solution of the iodine has been effected, the liquid is poured from the Erlenmeyer flask into a liter flask and made up to the 1000 c.c. mark with water. The potassium iodide is used simply to aid in the solution of the iodine; it takes no part whatever in the chemical changes caused by the iodine solution during titration. This solution should be kept in well-stoppered containers in a cool place.

A centinormal iodine volumetric solution, prepared by diluting the decinormal with nine times its volume of water, or by dissolving one-tenth the quantities of iodine and potassium iodide ordered for a liter of the decinormal solution, is used for the estimation of hydrogen sulphide in water. (See page 301.)

The substances given in the following list are estimated by means of decinormal iodine volumetric solution. The iodine acts as an oxidizing agent when brought into contact with these substances in aqueous solution ; under such circumstances it decomposes water as follows :

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* *Preparation of Pure Iodine.*—The United States Pharmacopœia directions for preparing pure iodine are as follows. "Heat powdered iodine in a porcelain dish placed over a boiling water-bath, and stir it constantly with a glass rod, so that the adhering moisture, together with any cyanogen iodide and most of the iodine bromide and chloride that may be present, may be vaporized. After twenty minutes transfer the iodine to a porcelain or other non-metallic mortar, and triturate it with about 5 per cent. of its weight of pure, dry potassium iodide, so as to decompose any remaining iodine bromide and chloride. Then return the mass to the dish, cover it with a clean glass funnel, and heat the dish on a sand-bath. Detach the sublimed, pure iodine, and keep it in well-stoppered bottles, in a cool place."

$$H_2O + I_2 = 2HI + O.$$

The oxygen thus set free at once reacts with the substance to be estimated. Since two iodine atoms are required to liberate one bivalent oxygen atom and combine with the two univalent hydrogen atoms, it follows that the normal iodine volumetric solution must contain an amount of iodine equal to the atomic weight of the element expressed in grammes.

The estimation of arsenic trioxide and antimony trioxide by means of iodine solution requires also the presence of sufficient alkali in the form of alkali bicarbonate to neutralize the hydriodic acid produced in the reaction. Alkali carbonates and hydrates destroy the color produced by the indicator, and on that account should not be used to supply the necessary alkali.

Starch test-solution is used as indicator with iodine volumetric solution ; the production of a blue color which does not disappear on stirring shows that sufficient iodine solution has been added.

One c.c. of decinormal iodine volumetric solution is the equivalent of:

	Gramme.
Iodine, I	0.012653
Arsenic Trioxide (arsenous acid), As_2O_3	0.004942
Potassium Sulphite, crystallized, $K_2SO_3.2H_2O$	0.009692
Sodium Bisulphite, $NaHSO_3$	0.005193
Sodium Thiosulphate, crystals, $Na_2S_2O_3.5H_2O$	0.024764
Sodium Sulphite, crystallized, $Na_2SO_3.7H_2O$	0.012579
Sulphur Dioxide, SO_2	0.003195
Antimony and Potassium Tartrate, crystals, $(K(SbO)C_4H_4O_6)_2.H_2O$	0.016560

The official sulphurous acid is assayed for sulphur dioxide by diluting a weighed portion of it with a large volume of distilled water, adding a few drops of starch test-solution, and titrating with decinormal iodine V. S. The sulphur dioxide is converted into sulphur trioxide (which in the presence of water becomes sulphuric acid) as follows :

$$H_2O + I_2 = 2HI + O.$$
$$SO_2 + O = SO_3.$$

Alkali sulphites, bisulphites, and thiosulphates are weighed, dissolved in water, and titrated with iodine in the presence of starch. The sulphites are converted into the corresponding sulphates by the oxygen from the water:

$$K_2SO_3.2H_2O + O = K_2SO_4 + 2H_2O.$$

The bisulphites are changed to bisulphates in the same manner:

$$NaHSO_3 + O = NaHSO_4.$$

Sodium thiosulphate is oxidized to sodium tetrathionate according to the equation:*

$$2Na_2S_2O_3.5H_2O + O = Na_2S_4O_6 + Na_2O + 10H_2O.$$

When arsenic trioxide is to be estimated its solution is prepared as follows. A weighed quantity of the substance and ten times as much sodium bicarbonate are warmed with water, 100 c.c. of the latter being used for each 0.5 gramme of arsenic trioxide taken. The mixture is allowed to cool and is then titrated. The official solutions of arsenous acid and potassium arsenite are treated in a similar manner. A measured volume of either solution is taken, boiled for a few minutes with about one-tenth its weight of sodium bicarbonate, the solution then cooled, diluted with five times its volume of water, and titrated with the iodine solution. The reaction between the arsenic trioxide and the iodine results in the formation of arsenic pentoxide, which, in the presence of water, combines with some of the excess of alkali and becomes an alkali arsenate. The following equations express these changes:

$$2H_2O + I_4 = 4HI + O_2.$$
$$As_2O_3 + O_2 = As_2O_5.$$
$$4NaHCO_3 + 4HI = 4NaI + 4H_2O + 4CO_2.$$

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* The equations expressing the reactions between sodium thiosulphate and iodine in the presence of water are usually condensed into the following one, since the hydriodic acid which forms by the action of iodine on water at once reacts with the sodium oxide formed in the oxidation of the thiosulphate to tetrathionate regenerating water:

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

The several reactions are:

$$H_2O + I_2 = 2HI + O.$$
$$2Na_2S_2O_3 + O = Na_2O + Na_2S_4O_6.$$
$$Na_2O + 2HI = 2NaI + H_2O.$$

The water of crystallization need not be regarded in writing the reaction, unless the equivalent of the volumetric solution in crystallized thiosulphate is to be calculated from the equation.

Tartar emetic is dissolved in about 30 times its weight of water, the resulting solution mixed with twice its volume of a cold, saturated solution of sodium bicarbonate, a little starch test-solution added, and the mixture immediately titrated with the iodine solution. The antimony trioxide, in which form the antimony may be considered to exist in tartar emetic, is oxidized in the reaction to antimony pentoxide, which remains in the aqueous solution in the form of metantimonic acid or an alkali salt thereof. $(K(SbO)C_4H_4O_6)_2.H_2O$ may be looked upon as composed of $2KHC_4H_4O_6 + Sb_2O_3$, from which indeed it is prepared. The chemical changes which occur in the estimation may be represented thus:

$$2H_2O + I_4 = 4HI + O_2.$$
$$Sb_2O_3 + O_2 = Sb_2O_5.$$
$$Sb_2O_5 + H_2O = 2HSbO_3.$$
$$4NaHCO_3 + 4HI = 4NaI + 4H_2O + 4CO_2.$$

The important reactions which happen in the process may be illustrated by the following single equation:

$$(K(SbO)C_4H_4O_6)_2.H_2O + I_4 + 3H_2O = 4HI + 2KHC_4H_4O_6 + 2HSbO_3.$$

If there is a delay of a few minutes in titrating the mixture of the tartar emetic and sodium bicarbonate, a white precipitate of antimonous acid, H_3SbO_3, will commence to separate. If this precipitation begins the titration will not be successful, as the antimony trioxide must be in solution to be properly acted on by the iodine.

Decinormal Sodium Thiosulphate Volumetric Solution.

Containing 24.764 grammes of $Na_2S_2O_3.5H_2O$ *in 1 liter.*

30 grammes of crystallized sodium thiosulphate are dissolved in 1000 c.c. of water. 100 c.c. of decinormal iodine volumetric solution are placed in a beaker, and thiosulphate solution run in from a burette until the color of the iodine nearly disappears; a few drops of starch solution are then added, and then more of the thiosulphate, until the blue color is discharged.

The number of cubic centimeters of thiosulphate solution required are multiplied by 10, and the volume got as the product diluted to 1000 c.c. Another trial should be made with the diluted solution to prove that it is of the same strength as the decinormal iodine volumetric solution.

The substances estimated by means of sodium thiosulphate volumetric solution either contain free iodine, or develop it on the addition of potassium iodide alone, or on the further addition of hydrochloric acid; so that starch solution is used as an indicator. The starch should not be added, however, until most of the iodine color has been removed by the addition of the thiosulphate volumetric solution, as otherwise lumps of blue starch iodide, which are difficult to decolorize, will form in the solution.

The reaction which takes place between sodium thiosulphate and iodine is explained in the consideration of decinormal iodine volumetric solution. As two molecules of sodium thiosulphate are required to react with the one bivalent oxygen atom, the normal solution of sodium thiosulphate must contain a number of grammes of the salt equal to the molecular weight in order to have the strength equivalent to one atom of hydrogen.

One c.c. of decinormal sodium thiosulphate volumetric solution is the equivalent of:

	Gramme.
Sodium Thiosulphate, $Na_2S_2O_3.5H_2O$	0.024764
Bromine, Br	0.007976
Chlorine, Cl	0.003537
Iodine, I	0.012653
Iron, Fe, in ferric salts	0.005588

Iodine is dissolved in about sixty times its weight of water by the aid of three times its weight of potassium iodide.

For the estimation of the iodine in the tincture, a measured volume of the liquid is diluted with four times its volume of an 8 per cent. aqueous solution of potassium iodide; the presence of the potassium salt prevents the precipitation of iodine upon the addition of the water.

In the case of compound solution of iodine which already contains potassium iodide, a weighed quantity of the preparation is simply titrated, starch being used as indicator. The reactions which occur in the titration of iodine with sodium thiosulphate volumetric solution are obviously the same as those which happen in the titration of sodium thiosulphate with iodine volumetric solution, and described thereunder.

The estimation of chlorine and bromine in aqueous solution is accomplished by adding to a known weight of the liquid sufficient 10 per cent. potassium iodide solution to redissolve any iodine precipitated and make a perfectly clear solution. By using this quantity of potassium iodide solution the complete absorption of the chlorine or bromine is assured. Each atom of free chlorine or bromine liberates one atom of iodine, as follows:

$$2KI + Cl_2 = 2KCl + I_2.$$

If, therefore, the clear solution obtained by the addition of an excess of potassium iodide be titrated with the thiosulphate volumetric solution, and the equivalent of 1 c.c. of this solution in bromine or chlorine be used in the calculation of results, the percentage amount of the bromine or chlorine in the solution may be ascertained. In the estimation of the available chlorine in chlorinated lime and solution of chlorinated soda, the solution of the substance, after the addition of potassium iodide, is acidified with diluted hydrochloric acid. The Pharmacopœial method of assay and requirement for chlorinated lime is as follows: "If 0.354 gm. of chlorinated lime be thoroughly triturated with 50 c.c. of water and carefully transferred, together with the washings, into a flask, and then 0.8 gm. of potassium iodide and 5 c.c. of diluted hydrochloric acid added, the reddish-brown liquid, mixed, towards the end of the titration, with a few drops of starch T. S., should require, for complete decoloration, not less than 35 c.c. of decinormal sodium hyposulphite V. S. (each c.c. corresponding to 1 per cent. of available chlorine)." The requirements of the Pharmacopœia for solution of chlorinated soda are, that "if 6.74 gm. of the solution be mixed with 50 c.c. of water, then 2 gm. of potassium iodide and 10 c.c. of hydrochloric acid added, together with a few drops of starch T. S., it should require not less than 50 c.c. of decinormal sodium hyposulphite V. S. to discharge the blue or greenish tint of the liquid (each c.c. of the volumetric solution corresponding to 0.052 per cent. of available chlorine)."

In the last two estimations the hypochlorites are first decomposed by the hydrochloric acid, as illustrated by the following equation:

$$CaOCl_2 + 2HCl = CaCl_2 + H_2O + Cl_2.$$

The chlorine thus set free acts on the potassium iodide, liberating iodine and forming potassium chloride; the iodine is then reduced to hydriodic acid by the sodium thiosulphate, which in turn is oxidized to sodium tetrathionate, as shown elsewhere. The potassium iodide is added before the hydrochloric acid, so that none of the chlorine which is set free will be lost, but that all of it will be absorbed by the iodide with the liberation of a corresponding amount of iodine. In order to estimate the available chlorine in hypochlorites by this method, chlorates must be known to be absent, since these substances also yield chlorine upon the addition of hydrochloric acid, and on that account would make the result too high. Furthermore, when these chlorinated compounds are used as bleaching and disinfecting agents, they are mixed with water without the addition of hydrochloric acid. Under these conditions only the chlorine of the hypochlorite exerts an action, the chlorate remaining unchanged. For these reasons the process given on page 169 is usually used when chlorates are present, although if acetic acid be substituted for hydrochloric in the process just given, only the chlorine of the hypochlorite will be recorded, the chlorate being unaffected.

When metallic iron is to be estimated in solid ferric salts with sodium thiosulphate volumetric solution the following plan is pursued: 0.5588 gm. of the salt is dissolved in a glass-stoppered bottle (having a capacity of about 100 c.c.), in 15 c.c. of water and 2 c.c. of hydrochloric acid; after the addition of 1 gm. of potassium iodide, the mixture is kept for half an hour at a temperature of 40° C., then cooled, mixed, towards the end of the titration, with a few drops of starch T. S., and completely decolorized with decinormal sodium thiosulphate volumetric solution. The quantities and method prescribed in the foregoing directions answer for all official ferric salts except soluble ferric pyrophosphate and the citrates of iron with quinine and strychnine. The estimation of the iron in the last-named substances requires the separation of the alkaloids; a description of the process will be found under the assay of these salts on pages 223, 226. The variation from the stated quantities in the estimation of the iron in soluble ferric pyrophosphate consists in the use of 10 c.c. of hydrochloric acid instead of 2 c.c., and the addition of 40 c.c. of water for the quantity of salt given.

When 0.5588 gm. of ferric salt is taken for the estimation, each c.c. of the decinormal sodium thiosulphate volumetric solution indicates 1 per cent. of metallic iron.

The metallic iron contained in the official solutions of ferric salts and in the tincture of ferric chloride of the Pharmacopœia is estimated by the method just given for the solid salts. In the case of these liquids, 1.1176 gm. of the fluid are introduced into the glass-stoppered bottle, digested with the specified amounts of the given reagents, and subsequently treated in identically the same manner. Each c.c. of decinormal solution required indicates 0.5 per cent. of metallic iron, when 1.1176 gm. of the fluid are used for the estimation.

The possibility of estimating iron by the foregoing method depends upon the fact that, when a ferric compound is warmed with potassium iodide, the ferric compound is reduced to the corresponding ferrous compound, iodine being simultaneously liberated. The following equation illustrates the changes and shows that each atom of iodine which is liberated indicates the previous existence of one atom of iron in the ferric state:

$$Fe_2Cl_6 + 2KI = 2FeCl_2 + 2KCl + I_2.$$

The presence of acid facilitates the reaction. Hydrochloric acid is usually employed, but the substance need not be represented in the equation expressing the change, unless it is assumed to first convert the ferric salt, by separation of the acid contained in the latter, into ferric chloride, which would then react in the manner indicated by the equation.

If sufficient potassium iodide is employed, the iodine which is set free remains in solution.

In the titration of the iodine with sodium thiosulphate, the usual reaction takes place between these two substances. Only the ferric salt of ferric ammonium sulphate and of such mixtures as the official scale salts of iron takes part in the liberation of iodine; the alkali salts remain unaffected, at least so far as the necessary reaction of the process is concerned.

The estimation of metallic iron in the official reduced iron is sometimes done with decinormal sodium thiosulphate volumetric solution in order to confirm the assay of this substance by decinormal potassium permanganate volumetric solution. For the details of the method reference may be had to the description of the uses of the last-named volumetric solution.

Decinormal Arsenic Trioxide Volumetric Solution.

Containing 4.942 grammes of As_2O_3 *in 1 liter.*

The arsenic trioxide exists in this solution as an alkaline arsenite. The solution is prepared by dissolving 4.942 grammes of finely powdered, pure arsenic trioxide (or 5 grammes of the official arsenic trioxide) in about 250 c.c. of water by the aid of about 20 grammes of potassium or sodium bicarbonate. The mixture may be warmed to facilitate solution. After the substances have dissolved, the solution is mixed with an equal bulk of water, allowed to cool, and then made up to 1 liter with water. The solution must be titrated against decinormal iodine volumetric solution to make sure that its strength is correct. The reaction between arsenic trioxide and iodine and the conditions favorable to the same are discussed under the consideration of decinormal iodine volumetric solution. From the statements made in that place it will be seen that one molecule of arsenic trioxide requires four univalent atoms of iodine for complete oxidation; hence the number of grammes of arsenic trioxide that would be needed to make a liter of normal solution would equal a number one-fourth as great as that which expresses the molecular weight of arsenic trioxide.

This solution is used for the estimation of the available chlorine in chlorinated lime and soda when chlorates are present, for the reasons mentioned on page 167. The arsenic trioxide is not acted upon by the chlorates, but is oxidized to arsenic pentoxide by the oxygen of the hypochlorites.

$$2CaOCl_2 + As_2O_3 = As_2O_5 + 2CaCl_2.$$

As the reaction takes place in alkaline solution the arsenic pentoxide really exists in the form of an arsenate, as explained on page 163.

The solution is applied in the case of chlorinated lime as follows: 0.354 gramme of the sample is thoroughly triturated with 25 c.c. of water and carefully transferred, together with the washings, into a flask; a volume of arsenic trioxide solution known to be in excess is then introduced, a few drops of starch test-solution are added, and the contents of the flask titrated with decinormal iodine volumetric solution until a permanent blue color is produced. As the arsenic trioxide and iodine solutions correspond to each other, volume for volume, the quantity of arsenic trioxide solution oxidized by the chlorinated lime may be found by deducting the number of cubic centimeters of the iodine solution required from the number of cubic centimeters of arsenic trioxide solution originally added. Each cubic centimeter f decinormal arsenic trioxide oxidized indicates 0.003537 gramme of available chlorine. Solution of chlorinated soda is examined in a similar manner.

It may sometimes be desirable to assay chlorinated lime and soda by both this method and the one given on page 166 in order to find the chlorine due to chlorate.

Decinormal Potassium Dichromate Volumetric Solution.

Containing 4.896 grammes of $K_2Cr_2O_7$ *in 1 liter.*

This solution is made by dissolving 4.896 grammes of pure potassium dichromate in about 500 c.c. of water in a liter flask, and then bringing the volume to 1000 c.c. by the addition of water. When made of this strength, the solution is the equivalent of equal volumes of decinormal potassium permanganate solution, or, in the case of iodine liberated from potassium iodide, it is the equivalent of equal volumes of decinormal sodium thiosulphate volumetric solution.

The most important use to which potassium dichromate volumetric solution is put is the titration of iron in ferrous compounds. The solution acts by oxidizing the iron to the ferric condition, each molecule of the potassium dichromate furnishing, in the presence of acid, three atoms of oxygen (or six atoms of chlorine) for this purpose. The strength of the normal solution is derived from this fact, the molecular weight of potassium dichromate [$K_2Cr_2O_7 = 293.78$], expressed in grammes, being divided by six to make the strength of the solution equivalent to one hydrogen atom.

The decomposition of the dichromate in this capacity may be easily understood by considering the molecule of potassium dichromate, $K_2Cr_2O_7$, to consist of one molecule of potassium oxide, K_2O, and two molecules of chromic anhydride, CrO_3; also that in the presence of ferrous salts these two molecules of chromic anhydride give up three atoms of oxygen, and at the same time are reduced to form one molecule of chromic oxide, as follows:

$$2CrO_3 = Cr_2O_3 + O_3.$$

One atom of oxygen changes two atoms of iron from the ferrous to the ferric condition, as illustrated by the following reaction:

$$2FeO + O = Fe_2O_3.$$

Hence the three oxygen atoms from the one molecule of potassium dichromate (which is the least quantity that can take part in the reaction) will change six atoms of iron from the ferrous to the ferric state, and, therefore, change as many molecules of a ferrous salt as are required to supply the six atoms of ferrous iron.

The acid employed in the estimation is usually the one whose radical is present in the ferrous salt. Sufficient of it must be used to supply the amount required to form normal salts with the potassium, chromium, and ferric iron. The reaction in the titration of ferrous sulphate in the presence of sulphuric acid may be expressed compactly by the equation—

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O.$$

When ferrous chloride is oxidized to ferric chloride, the change may be looked upon as the simple addition of chlorine to the original molecule. This chlorine is derived from the action of the chromic anhydride on the hydrochloric acid, as follows:

$$2CrO_3 + 12HCl = Cr_2Cl_6 + 6H_2O + Cl_6.$$

Two atoms of chlorine may be assumed to oxidize two atoms of iron in ferrous chloride, according to the equation—

$$2FeCl_2 + Cl_2 = Fe_2Cl_6.$$

Or, ferrous chloride may be assumed to be a solution of ferrous oxide in hydrochloric acid, and the oxygen of the dichromate supposed to pass from this salt, or the chromic anhydride to the ferrous oxide changing it to ferric oxide, which in the presence of hydrochloric acid becomes ferric chloride. In either case the reaction may be summed up in the equation—

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 3Fe_2Cl_6 + 2KCl + Cr_2Cl_6 + 7H_2O.$$

One c.c. of decinormal potassium dichromate volumetric solution is the equivalent of:

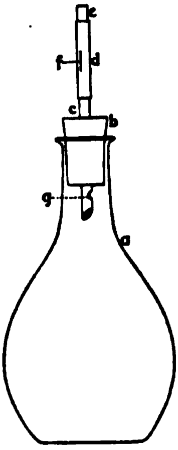
	Gramme.
Potassium Dichromate, $K_2Cr_2O_7$	0.0048963
Iron, in ferrous compounds, Fe	0.0055880
Ferrous Sulphate, anhydrous, $FeSO_4$	0.0151700
Ferrous Sulphate, crystallized, $FeSO_4.7H_2O$	0.0277420
Ferrous Sulphate, dried, $(FeSO_4)_2.3H_2O$	0.0178640

In order to estimate the ferrous iron in ferrous salts or determine the amount of real ferrous salt present with this volumetric solution, the salt is dissolved in water, acidified with acid, and the dichromate solution gradually added from a burette; a drop of the solution is occasionally withdrawn from the beaker by means of the glass rod and tested on a white porcelain surface with a drop of a freshly prepared solution of potassium ferricyanide, the addition of the volumetric solution being continued until a blue color is no longer obtained on the white surface.

For reasons given on page 176, however, the titration of ferrous iron is more easily conducted with potassium permanganate volumetric solution than with potassium dichromate volumetric solution.

When metallic iron is to be estimated it is dissolved in dilute sulphuric acid. Air must be excluded during the preparation of the solution, or oxidation to the ferric state will occur. By the use of the so-called Bunsen valve on the flask in which the solution is prepared air may be prevented from entering the vessel and the chances of oxidation reduced to a minimum. Fig. 12 shows the construction of the valve. *a* is a flask of convenient size; *b* a closely fitting stopper having a perforation, through which the glass tube, *c*, projects in both directions; the end of the tube inside the flask is ground to a point as illustrated, and a hole, *g*, is filed just above the pointed end. To the upper end of *c* is attached a piece of rubber tubing, *d*, through the wall of which, to one side of the diameter and in the direction of the length, the slit, *f*, has been cut; the upper end of *d* is closed with a plug of glass rod, *e*. After the apparatus has been constructed, the stopper, *b*, with its attachments is removed from the flask, a weighed quantity (about 1 gm.) of the iron to be estimated is introduced, and a sufficient quantity of dilute sulphuric acid (about 100 c.c.; made by pouring one volume of strong acid into five volumes of water) to dissolve it then poured in, and the stopper, *b*, reinserted. The flask and contents are then heated on an iron plate or sand-bath, the heat being gradually increased until the liquid is gently boiling. The steam from the boiling liquid and the hydrogen liberated from the sulphuric acid by the iron pass out through the slit, *f*. The object in grinding the tube, *c*, to a point is to prevent the drops of water which condense in the tube from being violently thrown out of the apparatus; while the hole, *g*, is filed just above the pointed end of *c* to permit the unobstructed passage of the vapor and gas. The heating is continued until the iron has completely dissolved. The flask is then allowed to cool, whereupon a par-

FIG. 12.



tial vacuum is produced within it, and the slit, *f*, which provided an exit for the steam and hydrogen, is closed by the external atmospheric pressure and the entrance of air thus prevented. When the contents of the flask have cooled to the ordinary temperature, the stopper, *b*, is removed, the solution of ferrous sulphate in the flask is diluted to a definite volume with water which has been previously boiled to expel oxygen and allowed to cool out of contact with air to prevent the absorption of oxygen; an aliquot part of the solution is then titrated with decinormal potassium dichromate volumetric solution in the usual way.

The iron of ferric salts may also be estimated by first reducing them to the ferrous condition and then oxidizing the iron with the potassium dichromate volumetric solution. The reduction to the ferrous state is effected by mixing the solution of the ferric salt with sulphuric acid and then adding a small piece of zinc; hydrogen is thus liberated, and the mixture is allowed to stand until a drop taken from the solution with a glass rod shows no red color upon a porcelain surface with a drop of potassium sulphocyanate test-solution. When the reduction is complete and the zinc has dissolved, the volume of the solution is adjusted, and an aliquot part titrated in the usual way.

Decinormal Potassium Permanganate Volumetric Solution.

Containing 3.1534 grammes of $K_2M_2O_8$ *in 1 liter.*

This solution is prepared by standardizing it with decinormal oxalic acid volumetric solution. For this purpose 3.5 grammes of pure, crystallized permanganate are dissolved in 1000 c.c. of recently boiled and cooled distilled water. 50 c.c. of the decinormal oxalic acid solution are placed in a beaker, 5 c.c. of concentrated sulphuric acid added, and the solution of permanganate carefully run into the mixture, while still warm, until a drop ceases to be decolorized after stirring, but imparts a pinkish tinge to the liquid. The number of c.c. of the permanganate solution used is multiplied by 20, and the number of c.c. of the liquid found as the product diluted to 1000 c.c. with recently boiled and cooled distilled water. A trial should be made to ascertain that 50 c.c. of the decinormal oxalic acid volumetric solution will destroy the color of exactly 50 c.c. of the permanganate solution.

This solution is liable to deteriorate on exposure or standing, and should therefore always be tested with the decinormal oxalic acid volumetric solution to verify its titer before use.

A solution which will hold its titer for a longer time may be made by the following process. 3.5 grammes of pure, crystallized potassium permanganate are placed in a flask, then 1000 c.c. of boiling water added, and the liquid boiled until the crystals are dissolved. The heat is then withdrawn and the flask closed and set aside in order to allow any suspended matter, such as manganese dioxide, to subside. Another solution is prepared in the same manner by dissolving 6.6 grammes of the potassium permanganate in 2200 c.c. of water. It also is set aside for insoluble substances to deposit. After the lapse of two days the clear portion of each solution is decanted into separate vessels provided with glass stoppers. The respective strengths of the two clear solutions are then determined by titration against the decinormal oxalic acid volumetric solution in the manner already described, and the solutions are finally mixed in such proportions that a given volume of the mixture will exactly correspond to an equal volume of the decinormal oxalic acid volumetric solution. The quantities required for this mixture may be found by alternate alligation. For example, let us suppose that 25 c.c. of the decinormal oxalic acid volumetric solution requires 24 c.c. of the stronger solution of potassium permanganate and 25.5 c.c. of the weaker solution. The quantity of the stronger solution needed would then lack 1 c.c. of the amount desired to react with the 25 c.c. of the oxalic acid solution, while the volume of the weaker solution would exceed the desired amount by 0.5 c.c. And, therefore, in order to dilute 24 c.c. of the stronger solution to the proper strength by the addition of the weaker solution, it will require for this purpose a quantity of the weaker solution equal to as many times the volume 25.5 c.c. as 0.5 c.c. is contained in 1 c.c. Thus, 51 c.c. of the weaker solution, equalling 50 c.c. of the decinormal oxalic acid volumetric solution, when mixed with 24 c.c. of the stronger solution, equalling 25 c.c. of the decinormal oxalic acid volumetric solution, make 75 c.c. of a solution of potassium permanganate, which equals 75 c.c. of the decinormal oxalic acid volumetric solution. The bulk of the two solutions is now mixed in the same proportion, 240 c.c. of the stronger and 510 c.c. of the weaker, or 480 c.c. of the stronger and 1020 c.c. of the weaker solution. After the mixture is thus prepared, a new trial should be made against the decinormal oxalic acid volumetric solution, to make sure that the correspondence is perfect.

The United States Pharmacopœia gives the following rule for obtaining the proportions in which the two solutions of potassium permanganate are to be mixed for the same purpose, when 10 c.c. of decinormal oxalic acid volumetric solution are used in the titration: "Deduct 10 from the number of c.c. of the weaker solution required to decompose 10 c.c. of decinormal oxalic acid V. S. With this difference multiply the number of c.c. of the stronger solution required for the same purpose. The product shows the number of c.c. of the stronger solution needed for the mixture.

"Next deduct the number of c.c. of the stronger solution required to decompose 10 c.c. of decinormal oxalic acid V. S. from 10, and with the difference multiply the number of c.c. of the weaker solution required for the same purpose. The product shows the number of c.c. of the weaker solution needed for the mixture.

"Or, designating by S the number of c.c. of the stronger solution, and by W the number of c.c. of the weaker solution required to decompose 10 c.c. of decinormal oxalic acid V. S., the following formula will give the proportions in which the solutions must be mixed:

Stronger Solution. Weaker Solution.

$$(W - 10)S + (10 - S)W."$$

Should the number of c.c. of decinormal oxalic acid volumetric solution used in the titration be other than 10, the abstract number 10, given in the foregoing rule and formula, must be replaced by the number representing the cubic centimeters of oxalic acid solution titrated with the potassium permanganate solutions.

The superior keeping quality of the potassium permanganate volumetric solution prepared in this manner is due to the fact that the salt is given ample opportunity to oxidize any impurities in the water, by the boiling and settling of the two solutions, and thus attain a stable condition before the strength of the volumetric solution is adjusted.

The strength of this solution is based on the fact that one molecule of potassium permanganate [$K_2Mn_2O_8 = 315.34$] in acid solution gives up five atoms of oxygen to certain oxidizable substances. Sulphuric acid is almost invariably the acid employed. This behavior of potassium permanganate may be conveniently explained by assuming the molecule of potassium permanganate to be composed of one molecule of potassium oxide, K_2O, and one molecule of permanganic anhydride, Mn_2O_7. The latter compound is the active part of the permanganate, and under the influence of certain reducing agents it splits up into manganous oxide and oxygen, as follows:

$$Mn_2O_7 = 2MnO + O_5.$$

The five atoms of oxygen set free in the reaction are taken up by the substance to be estimated, while the two molecules of manganous oxide and one molecule of potassium oxide from each molecule of permanganate dissolve in the sulphuric acid to form colorless potassium and manganous sulphates. Three molecules of sulphuric acid are therefore required for each molecule of potassium permanganate reduced in the estimation. The following reaction, which takes place in the standardization of the volumetric solution against decinormal oxalic acid volumetric solution, may be used to illustrate the behavior of potassium permanganate under the conditions named:

$$5H_2C_2O_4.2H_2O + K_2Mn_2O_8 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 18H_2O.$$

The carbon dioxide escapes from the solution with effervescence. Now, as five atoms of oxygen each with the valence two yielded by the permanganate equal ten univalent hydrogen atoms, it follows that a liter of decinormal potassium permanganate volumetric solution must contain a number of grammes of potassium permanganate equal to the hundredth part of the molecular weight of this salt.

As might be inferred from what has already been stated regarding the method of action of potassium permanganate, its solution is employed in the estimation of substances which are oxidizable by it. As these substances decolorize it when they reduce it, advantage is taken of its characteristic color in judging the end of the reaction, the appearance or disappearance of the color being noted as the case requires. From this same feature arises a preference of potassium permanganate volumetric solution to potassium dichromate volumetric solution for the titration of ferrous salts; the former solution imparts its own characteristic color to the solution when all of the iron has been changed to the ferric state, while the latter solution causes some of the ferrous salt to be lost by the repeated tests which are made to determine when the oxidation is complete.

One c.c. of decinormal potassium permanganate volumetric solution is the equivalent of:

	Gramme.
Potassium Permanganate, $K_2Mn_2O_8$	0.0031534
Barium Dioxide, BaO_2	0.008441
Calcium Hypophosphite, $Ca(PH_2O_2)_2$	0.0021209
Ferric Hypophosphite, $Fe_2(PH_2O_2)_6$	0.0020877
Iron in ferrous compounds, Fe	0.005588
Ferrous Carbonate, $FeCO_3$	0.011573
Ferrous Oxide, FeO	0.007195
Ferrous Sulphate, anhydrous, $FeSO_4$	0.015170
Ferrous Sulphate, crystals, $FeSO_4.7H_2O$	0.027742
Ferrous Sulphate, dried, $(FeSO_4)_2.3H_2O$	0.017864
Hydrogen Dioxide, H_2O_2	0.001696
Hypophosphorous Acid, HPH_2O_2	0.001647
Oxalic Acid, crystallized, $H_2C_2O_4.2H_2O$	0.006285
Oxygen, O	0.000798
Potassium Hypophosphite, KPH_2O_2	0.002598
Sodium Hypophosphite, $NaPH_2O_2.H_2O$	0.002646

The United States Pharmacopœia requires barium dioxide to respond to the following test: "If 2.11 gm. of barium dioxide be dissolved, as completely as possible, in ice-cold water to the volume of 25 c.c., with the aid of 7.5 c.c. of phosphoric acid, and 5 c.c. of this solution (corresponding to 0.422 gm. of the dioxide) be measured off for assay, it should require not less than 40 c.c. of decinormal potassium permanganate V. S. to impart to the liquid a permanent pink tint, corresponding to not less than 80 per cent. of pure barium dioxide (each c.c. of the volumetric solution indicating 2 per cent. of the latter)." In this estimation the barium dioxide is acted on by the phosphoric acid with the production of barium hydrogen orthophosphate and hydrogen dioxide, as follows:

$$BaO_2 + H_3PO_4 = BaHPO_4 + H_2O_2.$$

The hydrogen dioxide in contact with the potassium permanganate then decomposes into water and oxygen, according to the following reaction:

$$5H_2O_2 + K_2Mn_2O_8 + 3H_2SO_4 = 8H_2O + O_{10} + K_2SO_4 + 2MnSO_4.$$

One-half of the oxygen given off in the reaction comes from the hydrogen dioxide and the other half from the potassium permanganate.

The official valuation of solution of hydrogen dioxide reads as follows: "Dilute 10 c.c. of the solution with water to make 100 c.c. Transfer 17 c.c. of this liquid (containing 1.7 c.c. of the solution, assumed to weigh 1.7 gm.) to a beaker, add 5 c.c. of diluted sulphuric acid, and then, from a burette, decinormal potassium permanganate V. S., until the liquid just retains a faint pink tint after being stirred. Each c.c. of the decinormal potassium permanganate V. S. corresponds to 0.001696 gm. of absolute hydrogen dioxide. To express the strength of any solution of hydrogen dioxide approximately in volumes of available oxygen (that is, in volumes of oxygen, given off by 1 volume of the solution upon decomposition), multiply the number of c.c. of decinormal potassium permanganate V. S. decolorized by 1 c.c. of the solution, by 0.5594; or those decolorized by 1.7 c.c. of the solution, by 0.33. (It is assumed that 1000 c.c. of oxygen at 0° C. and 760 mm. pressure weigh 1.43 gm.).

"To express the strength in percentage (by weight) of absolute hydrogen dioxide, multiply the number of c.c. of decinormal permanganate V. S. decolorized by 1 c.c. of it, by 0.17; or divide the number of c.c. of permanganate V. S. decolorized by 1.7 c.c. of it, by 10." The reaction which takes place in this estimation is given under the valuation of barium dioxide.

The estimation of calcium hypophosphite is accomplished by dissolving 0.1 gm. of the salt in 10 c.c. of water, mixing the solution with 10 c.c. of sulphuric acid and 50 c.c. of decinormal potassium permanganate V. S., boiling the mixture for 15 minutes, and discharging the red color with decinormal oxalic acid V. S. The sulphuric acid first acts on the hypophosphite, liberating hypophosphorous acid and forming calcium sulphate, as follows:

$$Ca(PH_2O_2)_2 + H_2SO_4 = CaSO_4 + 2HPH_2O_2.$$

Then five (or a multiple of five) molecules of hypophosphorous acid react with two (or a multiple of two) molecules of potassium permanganate, and produce phosphoric acid in the following manner:

$$5HPH_2O_2 + 2K_2Mn_2O_8 + 6H_2SO_4 = 5H_3PO_4 + 2K_2SO_4 + 4MnSO_4 + 6H_2O.$$

The excess of potassium permanganate is then reduced by the oxalic acid of the decinormal solution, as already shown in an equation.

As the two volumetric solutions react with each other volume for volume, the number of c.c. of potassium permanganate solution actually required to oxidize the hypophosphite may be found by deducting the volume of oxalic acid solution required in the residual titration from the volume of potassium permanganate solution originally added.

Ferric hypophosphite is estimated in the same manner; the specified quantities of water, acid, and permanganate solution are used for 0.1 gm. of the salt. In the estimation of potassium and sodium hypophosphites the volume of sulphuric acid is decreased to 7.5 c.c., and the volume of permanganate solution to 40 c.c. for 0.1 gm. of either hypophosphite. To estimate diluted hypophosphorous acid, 0.5 gm. of the latter is mixed with 7 c.c. of sulphuric acid and 35 c.c. of decinormal potassium permanganate V. S., and treated according to the directions given for the estimation of calcium hypophosphite. The several varieties of ferrous sulphate are estimated by dissolving about 1.3871 gm. of the salt in about 25 c.c. of water, acidifying the solution with sulphuric acid, and adding decinormal potassium permanganate solution until the liquid acquires a permanent pink color. The iron of the ferrous sulphate is oxidized to the ferric condition by the oxygen from the potassium permanganate. As shown in the consideration of decinormal potassium dichromate volumetric solution, two atoms of iron are changed from the ferrous to the ferric state by one atom of oxygen. As one molecule of potassium permanganate contains five atoms of oxygen available for this purpose, it follows that one molecule will oxidize ten atoms of ferrous iron, or as many molecules of a ferrous salt as are required to supply these ten atoms. The reaction in the case of ferrous sulphate is as follows:

$$10FeSO_4 + K_2Mn_2O_8 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

Ferrous carbonate is dissolved in diluted sulphuric acid and titrated in the same manner. When this substance is to be estimated in the official saccharated ferrous carbonate or mass of ferrous carbonate, 1.1573 grammes of the sample are treated with distilled water, the insoluble matter collected on a plain filter and washed with distilled water until honey, sugar, or other soluble organic and inorganic substances which are liable to reduce potassium permanganate are removed. The filter and its contents are then transferred to a beaker, mixed with distilled water, and the mixture treated with diluted sulphuric acid until it acquires a distinct acid reaction and effervescence ceases. The contents of the beaker are then poured on another plain filter, and the pulp of the first filter washed on the same with distilled water until the washings fail to react with potassium ferricyanide test-solution. The mixed filtrate and washings are then titrated with decinormal potassium permanganate volumetric solution until a permanent pink tint is imparted to the liquid. When 1.1573 grammes of the sample are taken, each cubic centimeter of the solution represents 1 per cent. of ferrous carbonate.

Metallic iron may be dissolved for estimation in the apparatus shown in Fig. 12, according to the directions given on page 172. The iron of ferric salts may be reduced according to the method given on page 173, and then estimated by titration of the resulting ferrous compound with potassium permanganate volumetric solution in the usual manner.

The United States Pharmacopœia directs the estimation of the metallic iron in the official reduced iron to be conducted as follows: "Introduce 0.5588 gm. of reduced iron into a glass-stoppered bottle, add 50 c.c. of mercuric chloride test-solution, and heat the bottle, well stoppered, during one hour on a water-bath, frequently agitating. Then allow it to cool, dilute the contents with water to the volume of 100 c.c., and filter. To 10 c.c. of the filtrate, contained in a glass-stoppered bottle (having a capacity of about 100 c.c.), add 10 c.c. of diluted sulphuric acid, and subsequently decinormal potassium permanganate volumetric solution, until a permanent red color is produced. The number of c.c. of the volumetric solution required, when multiplied by ten (10), will indicate the percentage of metallic iron. To confirm the assay, decolorize the liquid by the addition of a few drops of alcohol, then add 1 gm. of potassium iodide, and digest for half an hour at a temperature of 40° C. The cooled solution, mixed with a few drops of starch test-solution, should require not less than 8 c.c. of decinormal sodium thiosulphate volumetric solution to discharge the blue or greenish color (each c.c. of the volumetric solution indicating 10 per cent. of metallic iron)."

The first step in the foregoing estimation is the solution of the iron. This is effected by the aid of the mercuric chloride test-solution, which dissolves only the metallic iron, leaving the oxides of iron unaffected. By its action the metal is converted into ferrous chloride in the following manner:

$$Fe_2 + 2HgCl_2 = 2FeCl_2 + 2Hg.$$

If hydrochloric or sulphuric acid were employed to bring the iron into solution, the ferrous oxide or ferrosoferric oxide which the reduced iron might contain would also be dissolved.

The iron of the ferrous chloride is then oxidized by the potassium permanganate to ferric chloride and ferric oxide, as follows:

$$30FeCl_2 + 3K_2Mn_2O_8 + 9H_2SO_4 = 10Fe_2Cl_6 + 5Fe_2O_3 3K_2SO_4 + 6MnSO_4 + 9H_2O.$$

The ferric oxide, however, at once reacts with some of the sulphuric acid present to form ferric sulphate, as follows:

$$5Fe_2O_3 + 15H_2SO_4 = 5Fe_2(SO_4)_3 + 15H_2O.$$

The last equation may therefore be combined with the preceding one and the two reactions compactly expressed in the following manner:

$$30FeCl_2 + 3K_2Mn_2O_8 + 24H_2SO_4 = 10Fe_2Cl_6 + 5Fe_2(SO_4)_3 + 3K_2SO_4 + 6MnSO_4 + 24H_2O.$$

The addition of sulphuric acid to the filtrate containing the ferrous chloride instead of hydrochloric acid is made on account of the fact that free hydrochloric acid has a reducing action on potassium permanganate, and is therefore liable to decolorize the volumetric solution after the ferrous iron has been completely oxidized.

The necessity of destroying the slight excess of potassium permanganate with which the liquid is tinted before undertaking to confirm the assay by digesting with potassium iodide and titrating with sodium thiosulphate volumetric solution arises from the fact that potassium permanganate as well as ferric iron liberates iodine from potassium iodide. Alcohol is employed to decolorize the liquid because it will reduce the potassium permanganate without affecting the ferric compounds; the alcohol is oxidized to aldehyde, which is without effect on the chemical changes brought about by the action of potassium iodide and sodium thiosulphate. The exact nature of the changes produced by the last two substances is fully explained under the consideration of the uses of decinormal sodium thiosulphate volumetric solution.

When oxalic acid is to be estimated by means of decinormal potassium permanganate volumetric solution, a weighed quantity of the substance is dissolved in about 15 times its weight of water, the solution mixed with one-tenth its volume of strong sulphuric acid, and, while still warm from the addition of the last, titrated with the potassium permanganate solution. Oxalates may be estimated by the same method with the use of twice the volume of acid.

Decinormal Silver Nitrate Volumetric Solution.

Containing 16.955 grammes of $AgNO_3$ *in 1 liter.*

This solution is prepared by dissolving 16.955 grammes of pure silver nitrate in sufficient distilled water to make exactly 1000 c.c. The solution should be preserved in small, glass-stoppered vials and light excluded.

Silver nitrate volumetric solution is used in the estimation of soluble bromides, chlorides, cyanides, iodides, and sulphocyanates. In all of these cases it acts by forming insoluble silver salts, one atom of silver combining with one atom of the halogen or one molecule of cyanogen or sulphocyanogen. As all of these substances are univalent, and as one molecule of silver nitrate contains one silver atom, the normal solution of silver nitrate is made by using the molecular weight of the salt in grammes. The reaction between the silver nitrate and the salt to be estimated results in the formation of an insoluble silver salt of the acid and a nitrate of the base used, thus:

$$KBr + AgNO_3 = AgBr + KNO_3.$$

One c.c. of decinormal silver nitrate volumetric solution is the equivalent of:

	Gramme.
Silver Nitrate, $AgNO_3$	0.016955
Ammonium Bromide, NH_4Br	0.009777
Ammonium Chloride, NH_4Cl	0.005338
Ammonium Iodide, NH_4I	0.014454
Calcium Bromide, $CaBr_2$	0.0099715
Ferrous Bromide, $FeBr_2$	0.010770
Ferrous Iodide, FeI_2	0.015447
Hydrocyanic Acid, absolute, HCN, with indicator	0.002698
Hydrocyanic Acid, absolute, HCN, to first formation of precipitate	0.005396
Hydriodic Acid, HI	0.012753
Hydrobromic Acid, HBr	0.008076
Lithium Bromide, LiBr	0.008677
Potassium Bromide, KBr	0.011879
Potassium Chloride, KCl	0.007440
Potassium Cyanide, KCN, with indicator	0.006501
Potassium Cyanide, KCN, to first formation of precipitate	0.013002
Potassium Iodide, KI	0.016556

	Gramme.
Potassium Sulphocyanate, KCNS	0.009699
Sodium Bromide, NaBr	0.010276
Sodium Chloride, NaCl	0.005837
Sodium Iodide, NaI	0.014953
Strontium Bromide, $SrBr_2$ (anhydrous)	0.012341
Strontium Iodide, SrI_2 (anhydrous)	0.017018
Zinc Bromide, $ZnBr_2$	0.011231
Zinc Chloride, $ZnCl_2$	0.006792
Zinc Iodide, ZnI_2	0.015908

The indicator usually employed with decinormal silver nitrate volumetric solution is potassium chromate test-solution, a few drops of which are added to the solution of the salt under examination.

On running in the silver nitrate solution from a burette, the first appearance of a permanent reddish color or precipitate of silver chromate is an indication of the end of the reaction. The applicability of this indicator depends upon the fact that, when a solution of silver nitrate is added to a solution containing either a bromide, chloride, cyanide, iodide, or sulphocyanate and a chromate, all of the other salt is decomposed with formation of insoluble silver salts having white or yellow colors, before the silver forms a permanent precipitate of red silver chromate. The reaction which then takes place is expressed by the following equation:

$$K_2CrO_4 + 2AgNO_3 = 2KNO_3 + Ag_2CrO_4.$$

The use of an indicator may be dispensed with if sufficient care is exercised to detect when a precipitate ceases to form. This result is attained by allowing the precipitate to subside after each addition of a small quantity of the volumetric solution. Rapid stirring or agitation will aid in the separation of the precipitate, and in some cases it is also necessary to apply heat.

When the substance to be estimated contains but one constituent capable of reacting with the volumetric solution, the result of the analysis is calculated in the usual way, as illustrated on page 152. If, however, it contains two or more constituents which are capable of acting upon the volumetric solution, this form of calculation cannot be applied.

This fact must be borne in mind when estimating the official bromides and iodides of ammonium, calcium, lithium, potassium, sodium, strontium, and zinc, all of which are liable, and some of which the Pharmacopœia allows, to contain the corresponding chloride. The following illustration will serve to explain the calculation needed in such cases. The Pharmacopœia directs that, "If 0.5 gm. of well-dried potassium bromide be dissolved in 10 c.c. of water, and 2 drops of potassium chromate T. S. be added, it should not require more than 42.85 c.c. of decinormal silver nitrate V. S. to produce a permanent red color of silver chromate (absence of more than 3 per cent. of chloride)."

If the result of this analysis was calculated in the usual way 0.5090 gm. of potassium bromide (0.011879 × 42.85) would be indicated. This amount, however, is 0.009 gm. in excess of the weight of the sample of potassium bromide originally taken. There are two possible explanations for this excess: one, a fault in the work; the other, the presence of some substance which, weight for weight, is capable of precipitating more silver nitrate solution than potassium bromide is. Potassium chloride is such a substance. And taking for granted that the analysis was accurately made on a perfectly dry salt otherwise known to be pure, the entire amount of this apparent excess of potassium bromide is attributable to the presence of potassium chloride, which substance, weight for weight, as shown by the equivalents of 1 c.c. of decinormal silver nitrate volumetric solution, precipitates more silver nitrate than potassium bromide does. The apparent excess of potassium bromide in the calculation is therefore due to the fact that every cubic centimeter of silver nitrate solution used in the analysis is assumed to precipitate 0.011879 gm. of potassium bromide, whereas in reality some part of the volume of the silver nitrate solution has precipitated potassium chloride in the smaller proportion of 0.00744 gm. per cubic centimeter.

The apparent excess of potassium bromide is therefore simply a multiple of the difference between the equivalent of potassium bromide and potassium chloride (0.004439), and the number of cubic centimeters of silver nitrate solution giving rise to it may obviously be found by dividing the excess (0.009 gm.) by the difference in the amounts of potassium bromide and potassium chloride equivalent to 1 c.c. of decinormal silver nitrate volumetric solution (0.004439 gm.). This number is 2.02. And, on account of the direct relation which the difference between the equivalents bears to the equivalent of potassium chloride (the presence of which substance necessitates the excessive quantity of silver nitrate), it follows that this number is also the number of c.c. of silver nitrate solution required to precipitate the potassium chloride present. If, then, this number of c.c.

(2.02) be deducted from the total number of c.c. (42.85) used in the analysis, the remainder (40.83) will be the number of c.c. of decinormal silver nitrate volumetric solution required to precipitate the potassium bromide present. The amount of each constituent may then be calculated in the usual way from the respective volume of decinormal silver nitrate volumetric solution required for its precipitation, as follows:

For potassium chloride—

.00744 × 2.02 = 0.01502 gm. KCl.

0.500 : 0.01502 : : 100 : 3.00 per cent. KCl.

For potassium bromide—

0.011879 × 40.83 = 0.48501 gm. KBr.

0.500 : 0.48501 : : 100 : 97.00 per cent. KBr.

When hydriodic acid is estimated by titration with silver nitrate solution, as in the official estimation of the pharmacopœial syrup of hydriodic acid, it is first neutralized with ammonium hydrate. Potassium chromate is used as indicator. In the cases of ferrous bromide and iodide, the use of potassium chromate as indicator is inadmissible on account of its reaction with the iron. The method of estimating these substances is illustrated by the official assays of saccharated ferrous iodide and syrup of ferrous iodide given on page 187.

With potassium cyanide and hydrocyanic acid the volumetric solution may be added, without the use of an indicator, until the formation of a permanent precipitate is observed, in which case just one-half the number of c.c. will be required as when the indicator is employed. The explanation of this behavior is, that when an alkali cyanide is brought in contact with silver nitrate a soluble double cyanide of silver and the alkali is first formed, or that the silver cyanide is held in solution by the unaltered part of the original cyanide until one-half of the cyanide has been combined with the silver. The reaction in the case of potassium cyanide is as follows:

$$2KCN + AgNO_3 = KNO_3 + (KCN.AgCN).$$

The double cyanide of potassium and silver remains in solution until another molecule of silver nitrate is added, when all of the cyanogen is precipitated in the form of silver cyanide, as follows:

$$(KCN.AgCN) + AgNO_3 = KNO_3 + 2AgCN.$$

Hydrocyanic acid is first mixed with an excess of potassium hydrate solution. On account of the alkaline reaction of potassium cyanide, difficulty is experienced in finding when the proper amount of alkali has been added to neutralize the acid. For that reason hydrocyanic acid is better estimated by the official method of assay for the diluted acid. This consists in mixing 1.35 grammes of the sample with sufficient water and magnesia to make an opaque mixture of about 10 c.c.; two or three drops of potassium chromate test-solution are added, and then decinormal silver nitrate volumetric solution run in from a burette until a red tint is produced which does not disappear on stirring. The hydrocyanic acid is neutralized by the magnesia with the production of magnesium cyanide, from which the acid radical is finally precipitated by the silver nitrate.

Potassium sulphocyanate is estimated with potassium chromate as indicator.

Decinormal Potassium Sulphocyanate Volumetric Solution.

VOLHARD'S SOLUTION.

Containing 9.699 grammes of KCNS *in 1 liter.*

10 grammes of crystallized potassium sulphocyanate are dissolved in 1000 c.c. of water. The strength of this solution is adjusted so as to correspond exactly with that of decinormal silver nitrate V. S. To make this adjustment, introduce into a flask 10 c.c. of decinormal silver nitrate V. S. together with 0.5 c.c. of ferric ammonium sulphate T. S. and 5 c.c. of diluted nitric acid. To this mixture carefully add the sulphocyanate solution from a burette until it produces a brownish-red tint which does not disappear on shaking. Note the number of c.c. of the potassium sulphocyanate solution used, and dilute the remaining solution so that equal volumes of this and of the decinormal silver nitrate V. S. will be required to produce the permanent brownish or reddish tint.

The reaction that takes place between the silver nitrate and potassium sulphocyanate is:

$$AgNO_3 + KCNS = AgCNS + KNO_3.$$

The silver sulphocyanate separates as a white precipitate. As soon as all of the silver has been converted into this insoluble compound, the potassium sulphocyanate acts upon the ferric ammonium sulphate, producing ferric sulphocyanate, which imparts a reddish color to the solution. The following equation shows the reaction :

$$Fe_2(NH_4)_2(SO_4)_4 + 6KCNS = Fe_2(CNS)_6 + (NH_4)_2SO_4 + 3K_2SO_4.$$

The diluted nitric acid is used to facilitate the separation of the silver sulphocyanate by the shaking.

The strength of the solution is based on the fact that the sulphocyanogen, CNS, which unites with the silver is univalent ; therefore the decinormal solution is made by taking one-tenth the molecular weight of the potassium sulphocyanate in grammes.

This volumetric solution is sometimes used for the estimation of soluble silver salts, but its chief use is in the estimation of the halogens in iron compounds, where it is used to determine the excess of the silver nitrate volumetric solution, which has been previously added to completely precipitate these substances. It is employed in these cases to circumvent the interference which is caused by the reaction of the chromate indicator with the iron. The estimations of saccharated ferrous iodide and of syrup of ferrous iodide are examples of residual titrations done with this volumetric solution.

The United States Pharmacopœia gives the following directions for determining the value of saccharated ferrous iodide : "If 1.5447 gm. of saccharated ferrous iodide be dissolved in about 20 c.c. of water, in a small flask, and to this solution be successively added, first, 22 c.c. of decinormal silver nitrate V. S., then 5 c.c. of diluted nitric acid and 5 c.c. of ferric ammonium sulphate T. S., it should not require more than 2 c.c. of decinormal potassium sulphocyanate V. S. to produce a reddish-brown tint which persists after shaking (corresponding to about 20 per cent. of pure ferrous iodide)." *

The official process for assaying syrup of ferrous iodide and the requirement of strength are as follows : "If 1.5447 gm. of the syrup and 10 c.c. of water be introduced into a flask, and the liquid mixed, successively, with 11 c.c. of decinormal silver nitrate V. S., and 5 c.c., each, of diluted nitric acid and ferric ammonium sulphate T. S., it should not require more than about 1 c.c. of decinormal potassium sulphocyanate V. S. to produce a reddish-brown tint which persists after shaking (corresponding to about 10 per cent. of ferrous iodide)."

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* See explanatory note on page 317.

In these estimations the first reaction results in the formation of insoluble silver iodide and soluble ferrous nitrate, as follows:

$$FeI_2 + 2AgNO_3 = Fe(NO_3)_2 + 2AgI.$$

The excess of silver nitrate then reacts with the potassium sulphocyanate, the silver being precipitated as silver sulphocyanate, thus:

$$AgNO_3 + KCNS = AgCNS + KNO_3.$$

As soon as all of the silver has been removed from the solution in this manner, the slightest excess of potassium sulphocyanate reacts with the ferric salt used as indicator, as shown elsewhere, producing the reddish-brown color of ferric sulphocyanate.

Besides aiding in the separation of the silver sulphocyanate as already described, the nitric acid decreases the liability of the silver compounds to reduction in the foregoing estimations.

One c.c. of decinormal potassium sulphocyanate volumetric solution is the equivalent of:

	Gramme.
Potassium Sulphocyanate, KSCN	0.009699
Silver, Ag	0.010766
Silver Nitrate, AgNO3	0.016955

Decinormal Sodium Chloride Volumetric Solution.

Containing 5.837 grammes of NaCl *in 1 liter.*

To prepare this solution, dissolve 5.837 grammes of pure sodium chloride in enough water to make, at 15° C., exactly 1000 c.c.

Pure sodium chloride may be prepared by passing a current of dry hydrochloric acid gas into a saturated aqueous solution of the purest commercial sodium chloride, separating the crystalline precipitate, and drying it at a temperature sufficiently high to expel all traces of free acid. In place of this, transparent crystals of pure rock salt may be employed.

Sodium chloride volumetric solution is used to estimate soluble silver salts. It acts by giving up its chlorine to form insoluble silver chloride. The normal solution is on that account made to contain the molecular weight of the sodium chloride in grammes of the substance. The volumetric solution is added from a burette until a drop ceases to cause further precipitation in the silver solution; or, a measured volume of the decinormal sodium chloride solution which is known to be in excess is run into the solution of the silver salt, a few drops of potassium chromate test-solution added, and the excess of the decinormal sodium chloride volumetric solution found by residual titration with decinormal silver nitrate volumetric solution until a permanent red color is imparted to the liquid.

The former method is directed by the Pharmacopœia for the estimation of silver nitrate, while the latter method is ordered by the same authority in the estimation of the official diluted and moulded silver nitrates. The principle of the former method was long ago proposed as a substitute for the assay of silver by cupellation. In this process the silver is dissolved in nitric acid, a known quantity of sodium chloride in solution is added to the solution of the silver nitrate contained in a bottle, the latter is then well shaken to make the silver chloride settle clear, and the small amount of silver which still remains in solution is precipitated by the addition of small successive portions of a solution of sodium chloride having one tenth the strength of the solution first applied. This method is employed in the United States mints for the assay of silver.

One c.c. of decinormal sodium chloride volumetric solution is the equivalent of:

	Gramme.
Sodium Chloride, $NaCl$	0.005837
Silver, Ag	0.010766
Silver Nitrate, $AgNO_3$	0.016955
Silver Oxide, Ag_2O	0.011564

Decinormal Bromine Volumetric Solution.

KOPPESCHAAR'S SOLUTION.

Containing 7.976 grammes of Br *in 1 liter.*

This solution does not contain bromine in the free state, but yields it upon the addition of hydrochloric acid. To prepare the solution, dissolve 3 grammes of sodium bromate and 50 grammes of sodium bromide (or 3.2 grammes of potassium bromate and 50 grammes of potassium bromide) in enough water to make 900 c.c. Of this solution transfer 20 c.c. into a bottle having a capacity of about 250 c.c. and provided with a glass stopper; add 75 c.c. of water, next 5 c.c. of pure hydrochloric acid, and immediately insert the stopper. Shake the bottle a few times, then remove the stopper and quickly introduce 5 c.c. of potassium iodide test-solution, taking care that no bromine vapor escape, and immediately stopper the bottle. Agitate the bottle thoroughly, remove the stopper and rinse it and the neck of the bottle with a little cold water from the wash-bottle so that the washings flow into the bottle, and then add from a burette decinormal sodium thiosulphate volumetric solution until the iodine tint is exactly discharged, using towards the end a few drops of starch test-solution as indicator. Note the number of c.c. of the sodium hyposulphite volumetric solution thus consumed, and then dilute the bromine solution so that equal volumes of it and of decinormal sodium hyposulphite volumetric solution will exactly correspond to each other under the foregoing conditions.

The first reaction to occur in the standardization of this solution consists in the formation of bromic acid and hydrobromic acid from the bromate and bromide of sodium by the hydrochloric acid, as follows:

$$NaBrO_3 + HCl = HBrO_3 + NaCl.$$
$$NaBr + HCl = HBr + NaCl.$$

The bromic and hydrobromic acids then react in the following manner with the liberation of bromine:

$$HBrO_3 + 5HBr = 3H_2O + 3Br_2.$$

The bromine thus liberated decomposes the potassium iodide, setting iodine free, and forming potassium bromide, according to the following reaction:

$$2KI + Br_2 = 2KBr + I_2.$$

Each atom of bromine liberates one atom of iodine; the latter then acts on the sodium thiosulphate of the volumetric solution in the presence of water, as shown in equations given under the consideration of the volumetric solution of iodine.

As bromine acts indirectly through the liberation of iodine from potassium iodide when used for volumetric analysis, and as one atom of bromine liberates one atom of iodine, the normal solution of bromine is made by using enough of the alkali bromate and bromide in a liter of the solution to yield the atomic weight of bromine in grammes of the element upon the addition of hydrochloric acid.

The most important use of this volumetric solution is in the estimation of the pure phenol in commercial carbolic acid. A detailed description of its application in this connection is given on page 230.

One c.c. of decinormal bromine volumetric solution is the equivalent of:

	Gramme.
Bromine, Br	0.007976
Carbolic Acid, C_6H_5OH	0.001563

Alkaline Cupric Tartrate Volumetric Solution.

FEHLING'S SOLUTION.

The directions as laid down in the United States Pharmacopœia are the best to follow in the preparation of this solution. They are as follows:

"A. *The Copper Solution.*—Dissolve 34.636 gm.* of carefully selected, small crystals of pure cupric sulphate, showing no trace of efflorescence or of adhering moisture, in a sufficient quantity of water to make the solution measure, at or near 15°, exactly 500 c c.

"Keep this solution in small, well-stoppered bottles.

"B. *The Rochelle Salt Solution.*—Dissolve 173 gm. of potassium and sodium tartrate and 125 gm. of potassium hydrate in a sufficient quantity of water to make the solution measure, at or near 15°, exactly 500 c.c.

"Keep the solution in small, rubber-stoppered bottles.

"For use, mix exactly equal volumes of the two solutions at the time required."

The mixture constitutes the alkaline cupric tartrate volumetric solution; it owes its usefulness to the fact that it contains cupric oxide in alkaline solution, supposedly in the form of cupric tartrate. When a solution of cupric sulphate is mixed with a solution of potassium hydrate, a precipitate of cupric oxide is formed; but if tartaric acid or a salt of it (or certain other organic substances) is added to either solution, this precipitation will not take place, or, if it does occur, the precipitate will redissolve upon stirring. The result upon mixing the cupric sulphate and potassium hydrate solutions in the presence of the substances named is a clear, blue liquid. This solution is used both as a qualitative and quantitative test for glucose and certain other sugars, and also for substances which may be made to yield these sugars by treatment with acids.

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* The United States Pharmacopœia directs 34.640 grammes; but a calculation of the quantity, using the atomic weights given in the Pharmacopœia, will show that the figures in the text are correct.

The value of it for both uses depends upon the action of the sugars on the cupric oxide. The latter in alkaline solution oxidizes the sugar, and if only fixed alkali is employed, a red precipitate of cuprous oxide resulting from the reduction of the cupric oxide is thrown down; this behavior forms the basis of the employment of the solution as a qualitative test for the substances named,—if sufficient of the latter is added the blue color of the solution may be entirely destroyed, since its intensity is diminished as the extent of the reduction of the cupric oxide, to which the color is due, increases. The applicability of the solution for the estimation of glucose is due to the circumstances that one molecule of glucose has the power of reducing five molecules of cupric oxide to cuprous oxide, and that this alteration is attended by the disappearance of the blue color of the solution or by the formation of a precipitate; the use of the solution for volumetric processes is possible on account of the decoloration, and for the gravimetric method because of the formation of a precipitate. Among the products of oxidation are formic, acetic, tartronic, and other acids, but the characters of the other products of the change are not sufficiently understood to permit of the reaction being expressed in an equation.

The reducing powers of the other substances on the volumetric solution are given in the list of equivalents on page 194. Since cupric sulphate can be obtained perfectly pure in a crystallized condition, it is a convenient form in which to supply the cupric oxide.

As a molecule of cupric sulphate represents a molecule of cupric oxide, one molecule of anhydrous glucose [$C_6H_{12}O_6 = 179.58$], or its equivalent, will require five molecules of crystallized cupric sulphate [$CuSO_4.5H_2O = 248.80$] to obtain enough cupric oxide for complete oxidation. If the molecular weights of these substances be expressed in grammes, it will be seen that 179.58 grammes of glucose need 1244 grammes of crystallized cupric sulphate. The strength of the alkaline cupric tartrate volumetric solution is fixed so that 1 c.c. of it will require 0.005 gramme of glucose for complete reduction. A liter of the solution would therefore equal 5 grammes of glucose. To find the number of grammes of crystallized cupric sulphate needed to supply the cupric oxide necessary to oxidize this weight of glucose, and, on that account, required for a liter of the finished volumetric solution, the following proportion is employed:

$$179.58 : 5 :: 1244 : 34.636.$$

34.636 grammes of crystallized cupric sulphate are therefore required for one liter of alkaline cupric tartrate volumetric solution. As this number of grammes of cupric sulphate, which is the active reagent, has no simple relation to the number expressing the molecular weight of the substance, this volumetric solution is called an empirical volumetric solution. The uses of the potassium and sodium tartrate and of the potassium hydrate have been sufficiently explained in the foregoing treatment of the subject. The quantities of these substances called for by the directions for the preparation of this solution have been arrived at through experiment. They are not based on molecular quantities taking part in a reaction; the quantity of cupric sulphate is, however, derived from such a source, as has been shown, and for that reason care must be taken to use the pure salt and to accurately weigh the stated amount.

If *the copper solution* and *the Rochelle salt solution* are preserved separately in the manner directed, their qualities will remain unimpaired for a long time; but if the two solutions are mixed and the product allowed to stand for any great period before use, deterioration is likely to take place. Solutions which have deposited red or yellowish-red precipitates of cuprous oxide upon standing are obviously unfit for quantitative testing, and may lead to error, if used for qualitative testing, by throwing down cuprous oxide upon boiling when reducing sugars are not present. A solution which has undergone this change should always be rejected, and a fresh one prepared. Every lot of the solution, even if freshly prepared, should for the reason given be carefully examined previous to use, whether for qualitative or quantitative analysis, to ascertain that it has not deteriorated or that it does not yield a precipitate of cuprous oxide when treated alone.

For this purpose a small portion of the solution is diluted with four volumes of water, boiled for a few minutes, and then set aside, that any cuprous oxide which forms may settle, and thus be the more readily detected by sight. Solutions which do not withstand this test without producing a red or reddish-yellow precipitate must be discarded.

When used as a qualitative test, the solution is boiled in the foregoing manner, and, if no precipitate is formed, a solution of the material to be tested is added in small portions, the boiling being continued for several minutes. If no distinct precipitate is obtained, set the vessel aside until cool, and then look closely to see if any cuprous oxide has settled.

One c.c. of alkaline cupric tartrate volumetric solution is the the equivalent of:

	Gramme.
Cupric Sulphate, crystallized, $CuSO_4.5H_2O$	0.03464
Cupric tartrate, $CuC_4H_4O_6.3H_2O$	0.03685
Glucose, anhydrous, $C_6H_{12}O_6$	0.00500
Maltose, $C_{12}H_{22}O_{11}$	0.00807
Milk Sugar, $C_{12}H_{22}O_{11}$	0.00678
Saccharose, $C_{12}H_{22}O_{11}$ (to be inverted)	0.00475
Starch, $C_6H_{10}O_5$ (to be inverted)	0.00450

When alkaline cupric tartrate volumetric solution is used for estimating glucose by the volumetric method, 10 c.c. of the solution is put into a porcelain dish, diluted with 40 c.c. of water, and rapidly heated to boiling with a small flame. The glucose solution is then added from a burette in portions of a cubic centimeter, and the contents of the dish boiled after each addition until the blue color is just discharged. This point is detected by inclining the dish, so that the color of the clear, supernatant liquid may be observed against the white porcelain. It is not likely that this point will be exactly hit in the first titration; it will more likely be overstepped. But an idea of the approximate volume of glucose solution necessary to effect decoloration will be gained, and this will serve as a guide in another titration to be conducted in a similar manner. In this second trial, a volume of the glucose solution equal to that used in the first trial minus one or two cubic centimeters is added at once to the boiling-hot volumetric solution, and, after boiling for a minute, the titration is continued by the addition of the solution of glucose in drops, with subsequent boiling, until the blue color is entirely removed. The necessity for this method of procedure is on account of the fact that if a solution of glucose or other reducing sugar be added in small quantities at a time to the volumetric solution, as in the case of an ordinary volumetric estimation, the amount of cupric oxide reduced by the first quantity added will be greater than that reduced by the same quantity in any subsequent addition. The object of the foregoing method is to supply at once, as near as it is possible, the requisite quantity of glucose to completely reduce the portion of volumetric solution taken, and by this means obviate any discrepancies which may occur in the results from unequal effects in the reduction of the cupric oxide.

The presence of the precipitated cuprous oxide makes it difficult to determine the exact point at which the color of the volumetric solution vanishes. On that account ammonium hydrate is sometimes added to the volumetric solution in order to hold the cuprous oxide in solution, and thus keep the liquid in the dish clear during the titration. A modification of Fehling's solution containing ammonium hydrate to prevent the precipitation of cuprous oxide is known as Pavy's solution. However, when ammonium hydrate is employed for the said purpose, the boiling and titration of the solution must be conducted out of contact of air, otherwise the cuprous oxide in the ammoniacal solution is liable to be oxidized and lead to error.

Another means of determining whether all of the copper has been reduced consists in filtering a portion of the contents of the dish, acidifying the filtrate with acetic acid, and adding a drop of potassium ferrocyanide test-solution, when, if no brownish or reddish precipitate of cupric ferrocyanide is obtained, the reduction of the cupric salt is known to be complete. But when the operator has gained a little experience with the process he will be able to quite correctly judge the end of the reaction by the disappearance of the blue color, without the necessity of resorting to these expedients.

For the titration from which the result is finally calculated the solution of glucose should not be stronger than 1 per cent.; this strength may be adjusted by dilution, if necessary, after the first trial of the glucose solution upon the alkaline cupric tartrate solution.

The method of calculating the results of an estimation of a sugar with alkaline cupric tartrate volumetric solution may be illustrated, in the case of glucose, as follows. As each c.c. of the volumetric solution equals 0.005 gramme of glucose, 10 c.c., which is the volume of this solution always employed, equal 0.050 gramme of the same substance; that is to say, will require 0.050 gramme of glucose for its complete reduction, which is indicated by decoloration. Now, let us suppose that if 1 gramme of the material to be estimated for glucose is contained in 100 c.c. of the solution used to decolorize the 10 c.c. of volumetric solution, and that 6 c.c. of the solution of the material were required for the last-named purpose, then these 6 c.c. must contain the required 0.050 gramme of glucose. But the total weight of the material to be estimated which is contained in 6 c.c. of its solution amounts to 0.060 gramme. The following proportion will then be required to find the percentage amount of the glucose present in the material under investigation :

0.060 : 0.050 : : 100 per cent. : 83.33 per cent.

The method of estimating maltose and milk sugar is the same in detail as that given for glucose.

Saccharose and starch must be inverted before they can be estimated with alkaline cupric tartrate volumetric solution. The process of inversion consists in heating the substances in aqueous solution with hydrochloric or other acid, whereby the elements of water are absorbed by the foregoing carbohydrates with the production of the molecule, $C_6H_{12}O_6$. As far as is known, the action of the acid is purely mechanical. To effect this change in the saccharose a weighed quantity of the substance is dissolved in water, the solution mixed with 10 per cent. of its volume of strong hydrochloric acid and heated to 70° for fifteen minutes. Starch is inverted by mixing about 2 grammes of the sample with 95 c.c. of water, in a flask of suitable size, adding 5 c.c. of concentrated hydrochloric acid, and, after attaching the flask to an upright condenser, heating the whole in a boiling water-bath for three hours. The contents of the flask gradually become clear as the treatment continues.

In all these cases the solution of the sugar should be allowed to cool, then be made alkaline with sodium carbonate, and adjusted to a definite volume, before being put into the burette for use. The details given for the estimation of glucose apply to the use of the solutions of inverted saccharose and starch.

In calculating the results of estimations of maltose, milk sugar, saccharose, and starch, the corresponding equivalents of 10 c.c. of the volumetric solution must, of course, be substituted for the 0.050 gramme of glucose shown in the example given for illustration.

Decinormal Mercuric Potassium Iodide Volumetric Solution.

MAYER'S SOLUTION.

Containing 39.199 grammes of* $HgI_2.2KI$ *in 1 liter.*

This solution is made by dissolving 13.527 grammes of pure mercuric chloride in 600 c.c. of water, and 49.668 grammes of pure potassium iodide in 100 c.c. of water. The two solutions are then mixed, and sufficient water is added to bring the volume to exactly 1000 c.c.

The exact reaction that occurs upon mixing the solutions as well as the composition of the mercury compound in solution is still unknown. The mercury is assumed, however, to exist in the form of $HgI_2.2KI$. If this assumption is correct, the reaction would ordinarily be as follows:

$$HgCl_2 + 4KI = HgI_2.2KI + 2KCl.$$

But the quantity of potassium iodide directed corresponds to six molecules instead of four, and it has been found that this quantity cannot be very much reduced in the decinormal solution. Furthermore, the reaction of the mercury salt with strychnine, which is one of the best-defined reactions produced by it, points to the formula $KI.HgI_2.3KI$ rather than to $HgI_2.2KI$. The strength of the normal solution is arbitrarily derived from the fact that the molecule $HgI_2.2KI$ contains one bivalent atom of mercury.

The solution of mercuric potassium iodide produces precipitates with a great many alkaloids, and is therefore used both in detecting and estimating the same. The solution of the alkaloid should, as far as possible, be deprived of other organic substances before the reagent is added, since certain other organic substances besides alkaloids yield precipitates with mercuric potassium iodide. The solution should always be distinctly acidified with hydrochloric or sulphuric acid, but must not contain alcohol, ether, or acetic acid. The addition of an excess of the reagent is to be avoided. The precipitates are curdy or flocculent, and usually have a yellowish-white color.

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* The quantities of mercuric potassium iodide, mercuric chloride, and potassium iodide here given are all slightly less than those stated in the United States Pharmacopœia; they have, however, been derived by calculation from the official atomic weights.

This solution is used in estimating a number of the alkaloids, as follows. A dilute solution of the alkaloid is distinctly acidified, placed in a beaker, and the volumetric solution run in from a burette so long as a distinct precipitate is produced. The end of the reaction is determined by pouring a few drops of the mixture upon a small filter, bringing a drop of the clear filtrate into contact with a drop of the reagent, on a piece of glass, over a black surface, and noting whether or not a cloudiness is produced. Before the end of the reaction is finally reached all the portions taken out must be washed back with water into the beaker. The end of the reaction is known when the reagent produces no further turbidity on the glass with a drop of the precipitate. The compounds formed by the reagent with the different alkaloids vary somewhat. Some have the composition $BHI.HgI_2$,—for example, strychnine; the compound with morphine is a mixture of $B(HI)_4.(HgI_2)_3$ and $B(HI)_6.(HgI_2)_3$; while with quinine it is not far from the composition $B_2(HI)_3.(HgI_2)_3$ (B represents the base, strychnine, morphine, or quinine). The amount of alkaloid precipitated by 1 c.c. of the volumetric solution cannot be calculated from the formula, but has been determined experimentally for each one.*

At the present time the following equivalents of 1 c.c. of decinormal mercuric potassium iodide volumetric solution are accepted as the best that are known:

	Gramme.
Mercuric Potassium Iodide, $HgI_2.2KI$	0.0392
Aconitine	0.0269
Atropine in 5 per cent. solution	0.0097
Berberine	0.0425
Brucine	0.0197
Cinchonine	0.0102
Coniine	0.0125
Emetine	0.0189
Hyoscyamine	0.00698
Morphine	0.020
Narcotine	0.0213
Nicotine	0.00405
Physostigmine	0.01375
Quinidine	0.0120
Quinine	0.0108
Strychnine	0.0167
Veratrine	0.0296

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* A full discussion of the compounds of this reagent with the alkaloids may be found in Prescott's "Manual of Organic Analysis."

In many cases a twentieth-normal solution is preferred to the decinormal one.

The estimation of alkaloids by means of mercuric potassium iodide affords results which are only approximate, even at the best, for they are influenced by many circumstances, prominent among which are the concentration of the solution of the alkaloid, the proportion of acid present, and the effect of an excess of the reagent. On account of these objectionable features the estimation of alkaloids by this solution has been to a large extent abandoned for methods effecting the estimation of these principles by titration with standard acid solutions; the official method of assaying extract of nux vomica given on page 224 is an example of such a method.

PART III.

PHARMACEUTICAL ASSAYING.

CHAPTER I.

ASSAY OF ORGANIC DRUGS AND THEIR PREPARATIONS.

PRELIMINARY CONSIDERATIONS.

A COMPLETE description of the methods employed in analyzing plants is beyond the scope of this book. For a full description of that subject the reader is referred to Dragendorff's treatise on plant analysis, and to the general scheme of plant analysis devised by H. B. Parsons.*

The general methods of estimating the amount or strength of some of the most important organic substances are given here, however, in the belief that, where an assay of a new drug or preparation for such principles is required, some one of these processes may be applicable to the case.

In addition, descriptions of the methods of determining the amount of moisture and ash in crude drugs and other organic substances are given.

Apparatus.—Such apparatus as has already been described in this work under gravimetric and volumetric operations is sufficient, except that occasionally an apparatus for continuous extraction will be found useful. One can choose any of the various forms of extraction apparatus offered by dealers, or he can readily construct one for himself if an upright condenser is at hand. For hot extraction the Soxhlet tube is about as satisfactory as any.

Reaction to Litmus Paper.—The effect of a pharmaceutical substance on the color of litmus paper is often taken into account as a means of proving identity, deciding quality, or detecting impurity. When the substance is in aqueous solution, or soluble in water, it is simply necessary to dip the litmus paper into the solution of the substance and, after allowing it to become thoroughly soaked, to withdraw it and observe the color, in order to detect any change from the original color. Substances which are insoluble in water, or immiscible with it, are sometimes shaken with water, the latter separated and tested in the foregoing manner; where hot water is better adapted it is employed; in other cases these substances are dissolved in alcohol or other solvent. When the latter means is employed, the litmus paper should be thoroughly moistened with water before introducing it into the liquid to be tested; if the liquid is immiscible with water, or only very sparingly soluble in it, the paper should be allowed to remain in the fluid for five or ten minutes.

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* American Journal of Pharmacy, 52, 210; Pharmaceutical Journal, Transactions [3], 10, 793.

Solvents.—Ether, alcohol, and chloroform are the solvents usually employed for the extraction of organic drugs; occasionally carbon disulphide, petroleum ether, amyl alcohol, and benzene will be found useful adjuncts to these. Various mixtures of the foregoing solvents are also at times employed. Water, acidulated water, and mixtures of alcohol and water are sometimes used. Acidulated water is used with the view to forming a soluble salt of the alkaloid. A mixture known as *Prollius' fluid*, and composed of 325 c.c. of ether, 25 c.c. of alcohol, and 10 c.c. of stronger ammonia water, is useful in extracting a number of drugs for the detection of alkaloids, glucosides, and other active principles. It is especially useful in the examination of a drug of unknown composition for alkaloids. The small quantity of alcohol aids in the penetration of the drug by the ether, through the greater solvent action of alcohol on the materials of the drug; the ammonia is intended to liberate the alkaloid from the acid with which it is combined in the drug, and the ether dissolves the free alkaloid. *Modified Prollius' fluid* is Prollius' fluid in which from 80 to 100 c.c. of the ether specified in the foregoing formula have been replaced by chloroform. Alkaloids in general may be tested for by macerating 10 grammes of the substance in fine powder with 100 c.c. of Prollius' fluid for twenty-four hours; 50 c.c. of the clear liquid are then withdrawn and thoroughly agitated in a separating funnel with 0.5 c.c. of diluted sulphuric acid and 10 c.c. of water.* The aqueous layer is separated and diluted with an equal bulk of water; the resulting solution is tested for the presence of an alkaloid by the application of the numerous alkaloidal reagents mentioned on page 738 of Volume I. Of these reagents, Mayer's solution (decinormal mercuric potassium iodide volumetric solution) may be applied either for qualitative or quantitative purposes, as described on page 197 of this volume.

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* See the directions for the use of immiscible solvents on page 202.

Use of Immiscible Solvents.—"It is a property of many alkaloids that they are soluble in certain liquids in which their salts are insoluble, while in other liquids the case is reversed. When such liquids are not miscible, the conditions are favorable to what has been called the 'shaking out' process of separation. In many cases the extraction or separation may be effected by shaking together the concentrated aqueous extract, to which a suitable alkaline precipitant has been added, and some solvent, such as chloroform, ether, benzene, benzin (petroleum ether), amyl alcohol, etc. The precipitated alkaloid is thus washed out of the aqueous solution, and is dissolved by the chloroform or other immiscible liquid employed. From the solution of the alkaloid thus obtained, the latter may again be abstracted by a dilute acid. In the Pharmacopœia, the only liquid which is directed as solvent for alkaloids in such assays is *chloroform*. The extraction is to be performed in a glass separator or separating funnel, which consists of an elongated (globular, cylindrical, or conical) glass vessel, provided with a well-fitting stopper and an outlet-tube containing a well-ground glass stop-cock.

"When the solution of an alkaloid, suitably prepared, is introduced into this vessel, and chloroform subsequently added, the latter, owing to its higher specific gravity, will form the lower layer. If the two layers are violently shaken together, there will often result an emulsion which will separate only slowly, and often imperfectly. This is particularly liable to happen when the aqueous liquid containing the alkaloid, either in suspension or in solution, is strongly alkaline, and when it has a high specific gravity. To avoid the formation of an emulsion, the extraction should be accomplished rather by rapid rotation and frequent inversion of the separator than by violent shaking. When an emulsion has formed, its separation may be promoted by the addition of more of the solvent, preferably somewhat heated, aided, if necessary, by the external application of a gentle heat (32° to 38°; the stopper being removed for the time being), or by the introduction of a small quantity of alcohol or of hot water. The separation of the two layers may also be promoted by stirring the lower, chloroformic layer with a glass rod and detaching from the walls of the separator the adhering drops of emulsion.

"On withdrawing the chloroform solution of an alkaloid from the separator, a small amount of the solution will generally be retained in the outlet-tube by capillary attraction. If this were lost, the results of the assay would be seriously vitiated. To avoid this loss several successive small portions of chloroform should be poured into the separator without agitation, and drawn off through the stop-cock to wash out the outlet-tube.

"Another source of loss is the pressure sometimes generated in the separator by the rise of temperature caused when an alkaline and an acid liquid are shaken together. On loosening the stopper the liquid which adheres to the juncture of the latter with the neck is liable to be ejected. This is best avoided by mixing the liquids at first by rotation (avoiding contact of the contents with the stopper), and allowing them to become cold before stoppering the separator.

"The same precautions should be observed when an alkali carbonate has been used, in place of a caustic alkali, for setting free the alkaloid. In this case the liquids should be cautiously and gradually mixed by rotation, and the separator should be left unstoppered until gas is no longer given off."—*United States Pharmacopœia.*

Immiscible solvents are frequently used in the foregoing manner to separate alkaloids from impurities which are extracted along with them from the drugs; examples of such use will be found on pages 208 and 212.

Glucosides and other *active principles* are frequently removed from the acid solutions obtained in these processes, just before making them alkaline for removal of alkaloids, by agitation with one or more immiscible solvents, as petroleum ether, benzene, or chloroform. According to Dragendorff ("Plant Analysis," page 49), petroleum ether will remove from acid solution small quantities of *salicylic acid* and *piperin*; it will also remove *benzoic acid*. The same authority gives the following substances as removable from acid solutions by benzene: *santonin*, *caryophyllin*, *cubebin*, *digitalin*, *cascarillin*, *elaterin*, *populin*, *colocynthin*, *quassin*, *ericolin*, *caffeine*, *piperin*, *colchiceine*, and *berberine*,—the last in small quantity only. He also gives the following list of principles removable from similar solutions by chloroform: *benzoic acid*, *saponin*, *senegin*, *æsculin*, *picrotoxin*, *helleborein*, *cinchonine*, *theobromine*, *papaverine*, *narceine;* it also removes the substances which are removable by petroleum ether and benzene. From alkaline solutions petroleum ether removes the following: *coniine*, *methyl coniine*, *nicotine*, *lobeliine*, *sparteine*, and small quantities of *strychnine*, *brucine*, *emetine*, *veratrine*, *sabadilline*, and *sabatrine*. Benzene removes, in addition to the above, *atropine*, *hyoscyamine*, *physostigmine*, *pilocarpine*, *gelsemine*, *quinidine*, *narcotine*, *codeine*, *thebaine*, *aconitine*, and *cinchonine* (a trace). In addition to these, again, chloroform extracts from alkaline solution *cinchonidine*, *cinchonine*, *quinine*, *papaverine*, *narceine*, and small quantities of *morphine*. Amyl alcohol removes *morphine* and *solanine* from alkaline solutions.

In general practice it will be found best to saturate the acidulated aqueous solution of the alkaloid with the solvent to be used in the extraction of the latter before liberating the alkaloid from its salt; this may easily be done by rotating the separating funnel containing its two liquids, for a few minutes, previous to adding the alkali. Such a course will usually prevent the formation of large lumps of precipitate,—when the alkaloid is liberated,—and, as no violent agitation, such as these masses sometimes require to bring about their solution, will be needed in the subsequent extraction of the alkaloid, the chances of the formation of an emulsion will be greatly reduced.

ESTIMATION OF MOISTURE IN ORGANIC DRUGS.

The estimation of the moisture in drugs is one of the simplest means employed to determine their quality. In the case of some official organic substances the United States Pharmacopœia limits the amount of moisture which shall be present. As a rule, this moisture may be determined as follows. A watch-glass, beaker, or crucible is accurately balanced and the weight noted. If, as is frequently the case, the substance is to be subsequently ignited to determine its inorganic constituents, a crucible will be most convenient; and a platinum vessel is preferable to a porcelain one. Into the weighed vessel is put a convenient bulk of the substance whose moisture is to be estimated, and the vessel with its contents balanced as before. The increase in weight shows the amount of substance put into the vessel; usually from two to five grammes will be found a convenient quantity. The vessel with its contents is now placed in an air-bath, the temperature of which has been brought to the required point, and left there for an hour or so. It is then removed, allowed to cool in a desiccator, and weighed. To make sure that the drying is complete, the vessel and its contents are again put in the air-bath at the same temperature for an hour, and, at the expiration of that time, again allowed to cool as before; after which they are weighed. If the weight is found to have been unaltered by the second exposure in the air-bath, the moisture is known to be completely expelled. In which case, the loss from the original weight of the vessel and contents is the weight of moisture in the quantity of substance taken. The percentage amount of moisture is then found by simple proportion. If the weight is found to be less upon the second weighing, the drying must be repeated with alternate weighings until loss in weight ceases to occur. The temperature to be employed will depend upon the nature of the substance to be dried. From 100° to 110° is a suitable temperature for most *crude organic drugs* and their *extracts*.

Since the estimation of moisture by noting the loss in weight which occurs upon drying would be vitiated by the presence of other volatile substances, which would also pass off, this method cannot be used when volatile oils and similar substances are present; and, indeed, in the presence of these substances there is no satisfactory means of directly estimating moisture. Thick viscid substances are taken in thin layers for drying. Solids, which melt upon the application of any considerable heat, are usually first dried at a low temperature and then gradually brought to the heat finally required. In some cases of this kind, for instance, in the following official estimation of water in soap, the substance is distributed over a diluting material in order to allow the moisture to readily escape: "On placing a small, weighed portion of soap, together with about 10 c.c. of alcohol, in a tared beaker containing sand, evaporating the resulting solution of the soap to dryness, and drying the residue at 110°, the loss of weight should not exceed 36 per cent."

After estimating the amount of a substance in a drug containing moisture, it is often desirable to know the amount of the substance in an absolutely dry drug, in order that a comparison of the respective values of specimens may be made. The calculation of this amount involves the percentage of moisture present in the drug; it may be explained by supposing an example. A sample of opium showing 10 per cent. of moisture contains 9 per cent. of morphine. How much morphine would the drug contain if the moisture were completely expelled? In this case the actual opium which yields the morphine amounts to 90 per cent., the other 10 per cent. of the sample being moisture. If the moisture is completely expelled, the product will contain 100 per cent. of opium, and will therefore contain a proportionately larger amount of morphine than was shown by the moist sample. Hence the exact percentage of morphine which it would then contain, or which the absolutely dry drug would represent, may be found by proportion as follows :

90 per cent. : 100 per cent. : : 9 per cent. : 10 per cent.

The estimation of the water of crystallization in some important organic substances is considered on page 138.

ESTIMATION OF ASH IN ORGANIC DRUGS.

The estimation of the inorganic constituents is an important matter in the examination of vegetable and animal substances, since it frequently affords a means of detecting the addition of fixed inorganic matter to such of these drugs as can be adulterated without producing an alteration in their appearance to the naked eye. It must always be remembered in judging the quality of a substance that volatile inorganic matters are not detected by this process ; they must, therefore, be sought and estimated by other means. The estimation of the ash is conducted as follows. A crucible, preferably of platinum, is balanced ; it is then half filled with the material to be examined, and the weight of the whole taken in order to find the quantity of material put into the crucible. If, however, a moisture estimation has been made on the substance, as is usually the case in a systematic examination of an organic drug, the dried residue in the crucible is used for the estimation of the ash. In either case, the crucible with its contents is placed over a Bunsen burner and cautiously heated, at first just sufficiently to subject the contents of the crucible to destructive distillation, but with a gradually increased temperature, until dull redness is reached. By this means the gases, which form upon the heating of the organic matter, escape from the crucible without taking fire, and, therefore, without causing a mechanical loss of inorganic material. The final heat should not exceed dull redness, or some of the constituents of the ash, such as the alkali chlorides, are liable to be volatilized. In all cases the ignition is continued until the carbon is completely consumed. It will be found advantageous to place the crucible in a slanting position upon the triangle, in order to facilitate the entrance of air into the vessel, and, as one portion of the contents is thoroughly burned, to rotate the crucible in order to bring another portion of the contents into closer proximity to the flame. It is seldom advisable to stir the contents of the crucible during the estimation of the ash; and where this is done the greatest care should be exercised to prevent loss of material. The color of the ash will depend, of course, upon the inorganic substances present. The unburnt carbon can usually be discerned, and, if heat alone is found to be insufficient to oxidize it, the aid of ammonium nitrate may be resorted to. To use this substance, allow the crucible to cool somewhat, then introduce some of the finely granular, fused substance, and again heat the crucible to dull redness. The nitrate supplies the carbon with sufficient oxygen to effect its oxidation, while the excess of the salt is volatilized by heat. Care must be used in applying this treatment, since a sudden heating of the nitrate may cause some of the ash to be thrown out of the crucible. It is hardly necessary to say that a preliminary experiment should be made with the ammonium nitrate to prove its complete volatility. When the removal of the carbon is to all appearances complete, the crucible is allowed to become cool in a desiccator, and is then weighed. The end of the process is determined, however, by reigniting the crucible and its contents for fifteen or twenty minutes, again cooling and weighing. If the weight is then found to be constant, the weight of the crucible deducted from that of the crucible and ash leaves the weight of ash in the quantity of material taken. The percentage amount is calculated by proportion. The ash may then be subjected to a qualitative analysis to ascertain its composition, and, if necessary, to a quantitative analysis to find the amount of each constituent. While this process serves to detect the presence of fixed inorganic matter, and the weight of the ash is usually taken into consideration, it does not necessarily follow that the substance weighed as ash originally existed in that same form in the organic substance ; for instance, if a sample of starch adulterated with magnesium carbonate is ignited, only magnesium oxide is obtained as ash, and, consequently, only its weight noted ; whereas the amount of actual impurity in the sample is greater. Regard must also be had for the presence of substances which gain in weight upon ignition. Thus it will be seen that experiments other than the ash determination may be necessary to decide the real amount of mineral matter present.

EXTRACTION OF ALKALOIDS BY LYONS' METHOD.

With many drugs extraction of the alkaloid may be conveniently effected by maceration with Prollius' fluid, the action of which is explained on page 201. For this purpose, 10 grammes of the substance in fine powder are placed in a flask, and 100 c.c. of Prollius' fluid added. After some agitation the whole is set aside for from twelve to twenty-four hours, with occasional shaking. 50 c.c. of the clear liquid are then removed with a pipette. This clear liquid may contain, besides the alkaloids, fats, waxes, resins, coloring matter, and other plant principles. To separate the alkaloid from these impurities, the clear liquid is treated in one of two ways. It is either evaporated until the ether and alcohol are removed, the residue then treated with 0.5 c.c. of dilute sulphuric acid and 10 c.c. of water, the liquid filtered into a separating funnel, the undissolved substances and the filter washed with water until free from acid, and the washings collected with the filtrate. The liquid in the separator is then agitated with two or three successive portions of ether of 10 c.c. each, to remove impurities; after separation of the last portion of ether, the aqueous solution is rendered alkaline with sodium or ammonium hydrate, or sodium carbonate, and shaken in a separating funnel with a mixture of 3 volumes of ether and 1 volume of chloroform; the ethereal portion is removed, and the aqueous solution shaken successively with two more portions of the mixture of ether and chloroform; the three ethereal solutions are mixed and evaporated to dryness, in a tared beaker, on a water-bath; any residue is weighed. Or the separation of the alkaloid from the impurities may be accomplished by taking 50 c.c. of the clear liquid from the flask containing the drug and Prollius' fluid, after maceration, and agitating it in a separating funnel with three successive portions, of 5 c.c. each, of water acidified distinctly with hydrochloric acid; the mixed acid solutions are placed in a separating funnel, washed once with 15 c.c. of ether, to remove the last traces of impurities; the ether is separated, and the acid solution, after being returned to the separating funnel, is rendered alkaline with ammonia water, and agitated with three successive portions of ether of 15 c.c. each; the mixed ethereal washings are evaporated in a tared beaker on a water-bath to constant weight.

The result in either case is the weight of alkaloid in 5 grammes of the drug. The foregoing processes are illustrations of the gravimetric methods of alkaloidal assaying.

After weighing, the alkaloidal residue may be dissolved in very dilute sulphuric acid, and titrated with decinormal mercuric potassium iodide volumetric solution according to the directions given on page 198. In some cases, the alkaloidal residue, after weighing, may be more advantageously dissolved in about 5 or 10 c.c. of pure alcohol, the resulting solution diluted with water until a slight turbidity is produced, and then titrated with decinormal hydrochloric or sulphuric acid volumetric solution, using either Brazil wood, cochineal, or hæmatoxylin test-solution as indicator. Another course, and one that is usually preferred, consists in dissolving the alkaloidal residue in an excess of the standard acid, and then, by residual titration with centinormal alkali volumetric solution, determining the volume of standard acid neutralized by the alkaloid. The process of estimating an alkaloid by titrating it with a volumetric solution is termed the volumetric method of alkaloidal assaying ; when the volumetric solution is a standard acid, the method is called acidimetric. An example of the acidimetric method will be found in the assay of extract of nux vomica.

In the estimation of volatile alkaloids, the mixed ethereal washings containing the alkaloid are not evaporated in a tared beaker on a water-bath, but, instead, are added at once to a definite volume of standard acid which is known to be in excess, the ether permitted to evaporate spontaneously, and the number of cubic centimeters of acid neutralized by the alkaloid found by residual titration with standard alkali.

Aconite leaves and *root** may be conveniently assayed by either alternative of the foregoing gravimetric method, or by the volumetric method. In the last-named process, 1 c.c. of decinormal acid volumetric solution is equal to 0.0647 gramme of the total alkaloids of aconite root, or 0.0445 gramme of the total alkaloids of aconite leaves.

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* Dr. Squibb's physiological test is a very good method, if not the best one, for deciding the quality of aconite root and leaves. It determines the power of the drug by noting the effects which this produces on the nerves of the tongue. It should always be tried in confirmation of the chemical assay. It is applied to the root as follows. 10 gm. of the root in No. 30 powder are percolated with alcohol. If the process is properly conducted, the root will be exhausted when 100 c.c. of percolate have been obtained. 10 c.c. of the percolate are put into sufficient water to make 600 c.c. of solution. The mouth is then well rinsed out, and 4 c.c. of the dilute solution are put into it, and this held in the anterior portion of the buccal cavity for exactly one minute. The solution is then ejected, and the mouth once more rinsed out. If the root be of good quality, the characteristic tingling sensation which aconite causes will be experienced in the tongue in a few minutes, and it will continue for half an hour or longer. The effect from aconite root should be well marked at a dilution of 1 : 600 or 1 : 700. That of aconite leaves should be felt at a dilution of 1 : 100. If the effect is greater or less than that expected, a second trial may be made, after an interval of several hours. Tinctures and fluid extracts of aconite root may be assayed by the same test. These are simply diluted with water so that 600 parts of the solution represent

Bloodroot and *coca* are assayed according to the details of the second method, using a mixture of 95 c.c. of petroleum ether, 4 c.c. of alcohol, and 1 c.c. of ammonia water, instead of Prollius' fluid, for exhausting the drugs. If the residue of alkaloid in the case of coca is titrated with acid, each cubic centimeter of decinormal acid neutralized is assumed to indicate 0.0303 gramme of cocaine.

Conium may be assayed by first extracting with Prollius' fluid in the usual way. Then, on account of the volatility of its alkaloid, 50 c.c. of the clear liquid are added to 10 c.c. of water, acidulated with sulphuric or hydrochloric acid, the ether evaporated, the solution filtered to remove insoluble matter, the filtrate, while still acid, agitated with ether in a separating funnel to remove the last traces of impurities, then made alkaline with sodium carbonate, and extracted with three successive portions of ether in the usual way; the mixed ethereal solutions are added to an excess (usually 10 c.c.) of decinormal acid volumetric solution, the ether allowed to evaporate, and the excess of acid titrated with centinormal alkali volumetric solutions, using hæmatoxylin as indicated. Each c.c. of decinormal acid volumetric solution neutralized by the alkaloid represents 0.0172 gramme of coniine.

Gelsemium and *quebracho* can be assayed by the second alternative; in the case of the former, petroleum ether is used, instead of ether, to wash the impurities from the acid solution of the alkaloid, previous to adding alkali in excess and removing the alkaloid by agitation with ether or a mixture of ether and chloroform.

Where the proportion of alkaloid in a drug is very small, it may be necessary to use larger quantities of the material for extraction. Alcohol of the specific gravity 0.820 is a useful and effective solvent in such cases. The alcohol is recovered by distillation,* the residue poured into acidulated water, and treated as in the foregoing process.

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one part of aconite root. Solid extract of aconite root is dissolved in diluted alcohol and the solution adjusted to the same strength. The solutions of the preparations of aconite leaves are adjusted to a strength of 1 : 100.

* When a liquid is to be freed from alcohol or other volatile menstruum, at a limited temperature, the evaporation may be conducted with less risk of injuring the product by using a vacuum-apparatus of suitable construction.

In place of the given weight of drug, the corresponding volume in cubic centimeters of *fluid extract*, or about the fifth part in weight of *solid extract*, is to be taken. Five or ten times as much *tincture* as of fluid extract is used for an estimation. Fluid extracts and tinctures are evaporated on a small quantity of clean oak-wood sawdust at a moderate temperature.* An excess of acetic acid must be added to solutions containing volatile alkaloids—*e.g.*, the preparations of conium—before evaporating in this manner. The solid extract is to be dissolved in dilute alcohol and the resulting solution evaporated on sawdust. The residues in all of these cases are treated as in the assay of the drug, and the results calculated from the quantity of original material taken.

EXTRACTION OF ALKALOIDS BY KELLER'S METHOD.

A very convenient method of extracting alkaloids from crude drugs for the purpose of estimation is that proposed by C. C. Keller. The finely powdered drug is first thoroughly dried at from 90° to 100°, then a weighed quantity of it is put into a flask or bottle of convenient size (from 200 to 250 c.c.), and covered with a known weight of plain ether, or, more frequently, with a mixture of ether and chloroform. After the contents of the flask have been vigorously shaken and allowed to macerate for some minutes, an excess of 10 per cent. ammonium hydrate (usually 10 grammes) is added, the mixture thoroughly shaken, and then allowed to macerate with frequent shakings for half an hour. Some additional ammonium hydrate or plain water is then added, and the vigorous shaking repeated. Through the presence of the water and by means of the agitation, the powder is caused to completely agglutinate, and the supernatant liquid, in consequence, becomes clear. The effect of the alkaline solvent is the same as in the case of Prollius' fluid (see page 201). A fractional part of the weight of the ether or mixture of ether and chloroform which was applied to the drug may then be decanted to a weighed flask, the solvent distilled off, the varnish-like residue dissolved in 10 c.c. of ether, the resulting solution evaporated, and the residue thoroughly dried on a boiling water-bath and weighed. But since the clear liquid is liable to contain, besides the alkaloids, the substances mentioned on page 208, in the description of the extraction by Lyons' method, the results got by simple evaporation of the clear liquid in the manner just described are usually high. Where practicable, it is considered more exact to dissolve the residue, which has been thoroughly dried on a boiling water-bath, in alcohol and titrate the alkaloid as described on page 209. In the performance of Keller's method, however, it is customary to separate the alkaloid from the impurities by transferring a definite weight of the alkaloidal solution to a separating funnel, and shaking this solution with three successive portions of from 0.5 to 1 per cent. hydrochloric acid. The portions of acid so applied measure 25, 15, and 10 c.c. in the order of their application. The acid liquids are mixed, the mixture made alkaline with ammonia water, and the alkaloid removed by shaking with several successive portions of plain ether, or a mixture of three parts by weight of chloroform and two parts by weight of ether. The several portions of solvent so applied are mixed, the whole filtered, if necessary, through a small filter wet with ether, the latter afterwards washed with some of the plain solvent, and the filtrate and washings evaporated. The residue is dissolved in ether, and the solution evaporated by means of a current of air; this treatment is repeated two or three times to insure the complete expulsion of the chloroform, the residue being finally dried for a quarter of an hour on a boiling water-bath; it is then allowed to cool and afterwards weighed. The result may then be calculated from the weight of the residue and the quantity of drug represented by the weight of solution taken for the assay from the maceration flask; or, if feasible, the residue may be dissolved in alcohol and titrated with standard acid, as directed on page 209. Sometimes it is desirable to free the drug from fat before extracting the alkaloid. For this purpose, a weighed quantity of the thoroughly dried and finely powdered drug is placed in a funnel, closed with a plug of cotton, and percolated with ether, until ten drops of the percolate evaporated on a watch-glass leave no residue. In these cases, however, regard must be had for the solvent action of the fat on the alkaloidal substances.

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* See foot-note on page 210.

Aconite leaves and *root*, *belladonna leaves* and *root*, *hyoscyamus*, *physostigma*, *pilocarpus*, *pomegranate bark*, *stramonium leaves* and *seed*, and *veratrum viride* may all be assayed by this method. A mixture of ether and chloroform, in the proportion of 100 grammes of the former and 25 grammes of the latter, is used to extract the leaf drugs, the quantities named being applied to from 10 to 20 grammes of the drug. For the other drugs a mixture, composed of 90 grammes of ether and 30 grammes of chloroform, is employed for from 10 to 20 grammes of the plant material.

The equivalents of decinormal acid volumetric solution in the total alkaloids of aconite root and leaves are given on page 210. 1 c.c. of decinormal acid volumetric solution neutralizes 0.0289 gramme of the mydriatic alkaloids of belladonna leaves and root.

Colchicum root and *seed* are also assayed by this method, with the use of the last-mentioned mixture of ether and chloroform. In these instances acetic acid is used, instead of hydrochloric acid, in separating the alkaloid from the impurities; and sodium carbonate is substituted for ammonium hydrate, in making the purified liquid alkaline to liberate the alkaloid, previous to the extraction of it from the aqueous solution by the use of the immiscible solvent.

Ipecac, *kola*, and *guarana* are assayed by treating 10 grammes of the substance, according to the usual details of the Keller method, with a mixture of 60 grammes of ether and 40 grammes of chloroform. The ipecac should be deprived of fat by the means described on page 212. When the alkaloidal residue in the case of ipecac is titrated, each cubic centimeter of decinormal acid volumetric solution neutralized by the alkaloids is taken to represent 0.0254 gramme of emetine.

Hydrastis is assayed by Keller's method with the use of plain ether instead of the mixture of ether and chloroform usually employed. The alkaloids are removed from the ethereal solution by agitation with successive portions of water acidulated with hydrochloric acid, and afterwards from the acid solution by making it alkaline with ammonium hydrate and shaking in the customary manner with ether, or a mixture of ether and chloroform. Of the three alkaloids, berberine, hydrastine, and canadine, contained in the residue, the hydrastine is considered as representing the medicinal value of hydrastis. The hydrastine may be separated from the other alkaloids and obtained in well-defined crystals by dissolving the residue in 8 c.c. of warm alcohol, adding 4 c.c. of ether, and gradually 20 c.c. of water, and setting the mixture in a cool place to crystallize. After twenty-four hours the hydrastine will be found separated as slightly yellowish-colored needles. These may be collected on balanced filters and washed with 6 c.c. of cold water, which have been previously used to rinse the vessel in which the crystallization was conducted. The washed crystals are dried at 100° and weighed. If they are subsequently dissolved in standard acid solution, and the excess of acid determined by residual titration with standard alkali, each cubic centimeter of decinormal acid volumetric solution neutralized by the alkaloid is considered to represent 0.0383 gramme of hydrastine.

In order to assay *galenicals* by Keller's method, they are prepared for extraction, by it, according to the directions given on page 211.

EXTRACTION OF ALKALOIDS BY LLOYD'S METHOD.

The following method has been proposed by J. U. Lloyd for assaying the *fluid extracts of aconite, belladonna, coca, hyoscyamus, ipecacuanha, nux vomica, coffee, tea, maté, guarana, and kola.* It may also be applied with fair accuracy to the corresponding drugs in fine powder. It is especially applicable to the assay of the fluid extracts of the caffeine-containing drugs named. Its outlines are as follows. 5 c.c. of fluid extract are mixed in a mortar with an excess (2 c.c.) of official solution of ferric chloride, which serves in many cases to separate the alkaloids from combination with the organic acids of the drug and form chlorides. Sodium bicarbonate in powder is then carefully added in small portions, with constant stirring, until a stiff magma results; the stirring is continued until effervescence ceases. By using this amount the bicarbonate will be found to be in excess, and will then liberate the alkaloids from their chlorides or other salts. It will also precipitate the excess of iron as ferric hydrate, which substance, together with the excess of bicarbonate, retains the gums, proteids, tannins, coloring and other extractive matters of the fluid extracts. The magma is then triturated with four successive portions of chloroform of 10 c.c. each. These are decanted in succession into a weighed beaker and evaporated by placing the beaker on a water-bath whose temperature is kept below the boiling point of chloroform. When all the solvent has evaporated, the residue of alkaloid is completely dried by bringing the water-bath to boiling. The beaker is kept for fifteen minutes at this temperature. It is then wiped dry, allowed to cool, and is weighed with its contents. The drying is then repeated for fifteen minutes, to insure complete expulsion of chloroform, and if the weight is the same as at the previous weighing, the result is calculated into percentage by proportion between 5 grammes (the assumed weight of the 5 c.c. of fluid extract) and the weight of alkaloid found.

Preparations containing fat will yield the alkaloids contaminated with this principle. For purification, the residue of alkaloid is treated with water acidulated with dilute sulphuric acid, and the solution agitated with successive portions of ether to remove fat. The aqueous liquid is then rendered alkaline with ammonia water, and the alkaloids extracted by agitation with successive portions of chloroform, which, as before, are separated, mixed, and evaporated, in order to reobtain the alkaloid. The result should then be calculated from the weight of purified alkaloid found. If the alkaloid is contaminated with chlorophyll, the latter may be separated by the same process.

EXTRACTION OF CAFFEINE BY SQUIBB'S METHOD.

The outlines of this method may be readily gathered from the following descriptions of the assays of tea and coffee made according to it. The method may also be applied to *guarana* and *maté*. The magnesium oxide liberates the caffeine from its combinations in the materials tested.

Assay of Tea.

10 grammes of coarsely powdered tea are intimately mixed in a mortar with 2 grammes of magnesium oxide. The mixture is added to 100 c.c. of boiling water, and the heat maintained at that temperature for five minutes. It is then poured on a filter and the residue washed with 50 c.c. of water, after which it is again stirred into 100 c.c. of boiling water. After boiling for a few minutes the mixture is filtered and the residue percolated with water until exhausted, using about 100 c.c., or making a total of about 350 c.c. of percolate. The weaker portion is evaporated first, the stronger added, and the whole concentrated to 20 c.c. The concentrated solution is transferred to a separator with a few cubic centimeters of water, and washed successively with three portions of chloroform of 20 c.c. each. The mixed chloroformic washings are concentrated in a tared beaker, on a water-bath, to constant weight.

Assay of Coffee.

The same process is employed in coffee as in tea, using a finer powder, until the final 20 c.c. of aqueous solution are obtained. Instead of attempting to wash out the alkaloid from this solution with chloroform, it is poured into 100 c.c. of alcohol to precipitate albuminous matter. The mixture is filtered, the precipitate washed with alcohol, and the filtrate and washings concentrated on a water-bath to 20 c.c.; after which it is washed with three successive portions of chloroform of 20 c.c. each, and the mixed chloroformic solutions concentrated in a beaker, on a water-bath, to constant weight.

Assay of Opium.

(*According to the U. S. Pharmacopœia of 1890.*)

Opium, in any condition to be valued, *ten grammes*	10 gm.
Ammonia Water, *three and five-tenths cubic centimeters* . .	3.5 c.c.
Alcohol,	
Ether,	
Water, each, *a sufficient quantity*.	

Introduce the opium (which, if fresh, should be in very small pieces, and if dry, in very fine powder) into a bottle having a capacity of about 300 c.c., add 100 c.c. of water, cork it well, and agitate frequently during twelve hours. Then pour the whole as evenly as possible upon a wetted filter having a diameter of 12 cm., and, when the liquid has drained off, wash the residue with water, carefully dropped upon the edges of the filter and the contents, until 150 c.c. of filtrate are obtained.

Then carefully transfer the moist opium back to the bottle by means of a spatula, add 50 c.c. of water, agitate thoroughly and repeatedly during fifteen minutes, and return the whole to the filter.

When the liquid has drained off, wash the residue, as before, until the second filtrate measures 150 c.c., and finally collect about 20 c.c. more of a third filtrate. Evaporate in a tared capsule, first, the second filtrate to a small volume, then add the first filtrate, rinsing the vessel with the third filtrate, and continue the evaporation until the residue weighs 14 gm. Rotate the concentrated solution about in the capsule until the rings of extract are redissolved, pour the liquid into a tared Erlenmeyer flask having a capacity of about 100 c.c., and rinse the capsule with a few drops of water at a time, until the entire solution weighs 20 gm. Then add 10 gm. (or 12.2 c.c.) of alcohol, shake well, add 25 c.c. of ether, and shake again. Now add the ammonia water from a graduated pipette or burette, stopper the flask with a sound cork, shake it thoroughly during ten minutes, and then set it aside, in a moderately cool place, for at least six hours, or overnight.

Remove the stopper carefully, and, should any crystals adhere to it, brush them into the flask. Place in a small funnel two rapidly-acting filters, of a diameter of 7 cm., plainly folded one within the other (the triple fold of the inner filter being laid against the single side of the outer filter), wet them well with ether, and decant the ethereal solution as completely as possible upon the inner filter. Add 10 c.c. of ether to the contents of the flask, rotate it, and again decant the ethereal layer upon the inner filter. Repeat this operation with another portion of 10 c.c. of ether. Then pour into the filter the liquid in the flask, in portions, in such a way as to transfer the greater portion of the crystals to the filter, and, when this has passed through, transfer the remaining crystals to the filter by washing the flask with several portions of water, using not more than about 10 c.c. in all. Allow the double filter to drain, then apply water to the crystals, drop by drop, until they are practically free from mother-water, and afterwards wash them, drop by drop, from a pipette, with alcohol previously saturated with powdered morphine.

When this has passed through, displace the remaining alcohol by ether, using about 10 c.c., or more if necessary. Allow the filter to dry in a moderately warm place, at a temperature not exceeding 60° C. (140° F.), until its weight remains constant, then carefully transfer the crystals to a tared watch-glass and weigh them.

The weight found in grammes, multiplied by 10, represents the percentage of crystallized morphine obtained from the opium.

In its normal, moist condition, opium should yield not less than 9 per cent. of crystallized morphine, when assayed by the foregoing process.

Powdered and deodorized opium, when assayed by the same process, should yield not less than 13 nor more than 15 per cent. of crystallized morphine.

In the foregoing assay the water dissolves extractive matter and the salts of the various alkaloids from the opium; these remain in solution during the evaporation of the aqueous liquid. Upon the addition of the excess of ammonium hydrate, the alkaloids are liberated from the acids (chiefly sulphuric and meconic) with which they are combined. The several alkaloids, with the exception, of morphine dissolve in the ether; the morphine is practically insoluble in the latter. By vigorous shaking of the aqueous liquid containing the free morphine with the excess of ether over that required to saturate the aqueous solution, crystallization of the alkaloid is hastened and the principle obtained in a purer condition than would otherwise be had. The alkaloid separates in a finely crystalline form; its complete crystallization requires several hours. The alcohol is added with a view to holding in solution certain extractive matters, which would otherwise be precipitated in the crystallization of the morphine and thereby cause a less pure alkaloid to be obtained.

The relatively large quantity of ether also counteracts the solvent action of the alcohol on the morphine, which effect, in the absence of ether, would be sufficient to prevent the separation of a considerable quantity of the morphine.

The addition of the two portions of ether of 10 c.c. each to the contents of the flask, the subsequent rotation of the latter, and the final decantation of the ether are simply to wash the crystals of morphine and the aqueous layer free from the last traces of other alkaloids.

The crystallized morphine weighed at the end of the operation has the formula, $C_{17}H_{19}NO_3.H_2O$.

Assay of Opium.

(*According to the U. S. Pharmacopœia of 1880.*)

Opium, in any condition to be valued	7 grammes.
Lime, freshly slaked	3 grammes.
Chloride of Ammonium	3 grammes.
Alcohol,	
Stronger Ether,	
Distilled Water, each, *a sufficient quantity*.	

Triturate together the opium, lime, and 20 c.c. of distilled water, in a mortar, until a uniform mixture results; then add 50 c.c. of distilled water, and stir occasionally, during half an hour. Filter the mixture through a plaited filter, three to three and one-half inches (75 to 90 mm.) in diameter, into a wide-mouthed bottle or stoppered flask (having the capacity of about 120 c.c. and marked at exactly 50 c.c.), until the filtrate reaches this mark.

To the filtered liquid (representing 5 grammes of opium) add 5 c.c. of alcohol and 25 c.c. of stronger ether, and shake the mixture; then add the chloride of ammonium, shake well and frequently during half an hour, and set it aside for twelve hours.

Counterbalance two small filters, place one within the other in a small funnel, and decant the ethereal layer as completely as practicable upon the filter. Add 10 c.c. of stronger ether to the contents of the bottle and rotate it; again decant the ethereal layer upon the filter, and afterwards wash the latter with 5 c.c. of stronger ether, added slowly and in portions. Now let the filter dry in the air, and pour upon it the liquid in the bottle, in portions, in such a way as to transfer the greater portion of the crystals to the filter. Wash the bottle, and transfer the remaining crystals to the filter, with several small portions of distilled water, using not much more than 10 c.c. in all, and distributing the portions evenly upon the filter. Allow the filter to drain, and dry it, first by pressing it between sheets of bibulous paper, and afterwards at a temperature between 55° and 60° C. (131° to 140° F.). Weigh the crystals in the inner filter, counterbalancing by the outer filter. The weight of the crystals in grammes, multiplied by *twenty*, equals the percentage of morphine in the opium taken.

In this method, the natural salts of the opium alkaloids are decomposed by the calcium hydrate (slaked lime), which serves the additional purpose of dissolving the morphine liberated in the reaction. By triturating together 7 grammes of opium and 70 c.c. of water, and taking 50 c.c. of the clear filtrate, the morphine present in 5 grammes of opium is obtained, without the trouble of repeatedly washing the insoluble matter of that quantity of opium to attain the same end. The filtrate may be conveniently measured by collecting it in a regular 100 c.c. cylinder. It is thence poured into an Erlenmeyer flask, and the cylinder rinsed by successively measuring in it the alcohol and ether, which are to be added to the aqueous calcium hydrate solution of the morphine. This process makes no allowance for the volume of the solvent being increased by any moisture in the drug or by taking solids into solution, and, for all practical purposes, the slight increases arising from these sources may be safely ignored. The addition of the ammonium chloride causes the liberation of the morphine from its solution in calcium hydrate, by reacting with the last-named solution to form calcium chloride, ammonia, and water. The functions of the alcohol and ether in the assay are explained on page 217. The crystallized alkaloid weighed has the composition $C_{17}H_{19}NO_3.H_2O$.

Assay of Extract of Opium.

(According to the U. S. Pharmacopœia of 1890.)

Extract of Opium,* *four grammes*	4 gm.
Ammonia Water, *two and two-tenths cubic centimeters* . . .	2.2 c.c.

Alcohol,
Ether,
Water, each, *a sufficient quantity.*

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* The words *extract of opium, dried at 100° C., four grammes*, which are given at this point in the Pharmacopœia, do not mean that, in the examination of a commercial extract, a portion of the sample is to be dried at 100° C., and that the amount specified in the assay is to be weighed off from such dried

Dissolve the extract of opium in 30 c.c. of water, filter the solution through a small filter, and wash the filter and residue with water, until all soluble matters are extracted, collecting the washings separately. Evaporate, in a tared capsule, first, the washings to a small volume, then add the first filtrate, and evaporate the whole to a weight of 10 gm. Rotate the concentrated solution about in the capsule until the rings of extract are redissolved, pour the liquid into a tared Erlenmeyer flask, having a capacity of about 100 c.c., and rinse the capsule with a few drops of water at a time, until the entire solution weighs 15 gm. Then add 7 gm. (or 8.5 c.c.) of alcohol, shake well, add 20 c.c. of ether, and shake again. Now add the ammonia water from a graduated pipette or burette, stopper the flask with a sound cork, shake it thoroughly during ten minutes, and then set it aside, in a moderately cool place, for at least six hours or overnight. From this point proceed as directed in the case of the assay of opium. The weight of crystals found, multiplied by 25, represents the amount of crystallized morphine obtained from 100 gm. of the extract. 100 gm. of the extract should yield 18 gm. of crystallized morphine.

For the explanation of this assay, see that given of assay of opium on page 217.

Assay of Tincture of Opium.

(*According to the U. S. Pharmacopœia of 1890.*)

Tincture of Opium, *one hundred cubic centimeters*	100 c.c.
Ammonia Water, *three and five-tenths cubic centimeters* .	3.5 c.c.
Alcohol,	
Ether,	
Water, each, *a sufficient quantity.*	

Evaporate the tincture to about 20 c.c., add 40 c.c. of water, mix thoroughly, and set the liquid aside for an hour, occasionally stirring, and disintegrating the resinous flakes adhering to the capsule. Then filter, and wash the filter and residue with water, until all soluble matters are extracted, collecting the washings separately. Evaporate in a tared capsule, first, the washings to a small volume, then add the first filtrate, and evaporate the whole to a weight of 14 gm. From this point proceed as directed in the case of the residue of the same weight in the assay of opium.

The weight found represents the amount of crystallized morphine obtained from 100 c.c. of the tincture. 100 c.c. of the tincture should yield from 1.3 to 1.5 gm. of crystallized morphine.

When *Tincture of Deodorized Opium, Tincture of Ipecac and Opium*

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material. These words are intended to express the requirements of the Pharmacopœia that an extract of opium, to be official, must be perfectly dry, and must in that condition yield 18 per cent. of crystallized morphine. If it is desired to find the amount of crystallized morphine which an extract containing moisture would represent, if completely dried, an estimation of its moisture is made by drying at 100°, and the quantity of crystallized morphine then calculated from the percentage found by assay of the original sample, according to the method described on page 205.

and Wine of Opium are to be assayed, the foregoing process and quantities are to be used. The strength of these preparations should be the same as that of the simple tincture.

In the assays coming under this heading the liquids are evaporated to expel alcohol, so that the addition of water will completely precipitate the resinous substances present; the explanation of the assay of opium given on page 217 deals with the further treatment of the evaporated liquid.

Assay of Vinegar of Opium.

(*According to L. F. Kebler.*)

The official directions for the assay of vinegar of opium are inapplicable on account of the presence of the relatively large quantity of sugar that the preparation contains. When this preparation is to be assayed, proceed as follows: Render 100 c.c. of the sample alkaline with ammonia water, add 2 c.c. of ether, shake vigorously for 10 minutes, and set aside for 6 hours or overnight. Collect the alkaloids upon a filter previously wetted with water, and wash them with a small quantity of water. Transfer the still moist precipitate to a small capsule, add 10 c.c. of 5 per cent. sulphuric acid, or enough to impart acidity, warm on the water-bath, cool, allow to stand for an hour or more, filter, and wash the filter and residue well with water. Mix the filtrate and washings, add 10 gm. of alcohol, shake, add 25 c.c. of ether, shake again, and, commencing with the addition of ammonia water until the solution is alkaline, follow the directions from a corresponding point given in the assay of opium according to the United States Pharmacopœia of 1890. 100 c.c. of the vinegar should yield from 1.3 to 1.5 gm. of crystallized morphine.

The treatment with ammonia water and saturation with ether causes the precipitation of the alkaloids. These are afterwards dissolved by the sulphuric acid, and the morphine precipitated for weighing under the usual conditions, whose essential features are explained on page 217.

Assay of Cinchona.

(*According to the U. S. Pharmacopœia of 1890.*)

I.—FOR TOTAL ALKALOIDS.

Cinchona, in No. 80 (or finer) powder, and completely dried at 100° C. (212° F.),* *twenty grammes* . . . . 20 gm.
Alcohol,
Ammonia Water,
Chloroform,
Ether,
Normal Sulphuric Acid V. S.,
Normal Potassium Hydrate V. S., each, *a sufficient quantity.*

To 20 gm. of cinchona, in very fine powder, and contained in a bottle provided with an accurately ground glass stopper, add 200 c.c. of a previously prepared mixture of 19 volumes of alcohol, 5 volumes of chloroform, and 1 volume of ammonia water, stopper the bottle, and shake it thoroughly and frequently during four hours. Then separate the liquid by pouring it into another bottle through a funnel containing a pellet of cotton, in such a manner that no material loss by evaporation may result.

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* This does not mean that, when a sample of cinchona is to be assayed, a portion of the sample should be dried at 100° C., and that the amount specified is to be weighed off from such dried material; on the contrary, it is

Transfer 100 c.c. of the clear filtrate (representing 10 gm. of cinchona) to a beaker, and evaporate it to dryness.

Dissolve the residue of crude alkaloids thus obtained in 10 c.c. of water and 4 c.c. of normal sulphuric acid V. S., with the aid of a gentle heat, filter the cooled solution into a separatory funnel, and wash the beaker and filter until the filtrate no longer has an acid reaction, using as small a quantity of water as possible.

Now add 5 c.c. of normal potassium hydrate V. S., or such an amount as will render the liquid decidedly alkaline, and extract the alkaloids by shaking the mixture, first with 20 c.c., and then repeatedly with 10 c.c., of chloroform, until a drop of the last chloroform extraction, when evaporated on a watch-glass, no longer leaves a residue. Evaporate the united chloroformic extracts in a tared beaker, dry the residue at 100° C. (212° F.), and weigh. The weight found in grammes, multiplied by *ten* (10), will give the percentage of *total alkaloids* in the specimen of cinchona tested.

The United States Pharmacopœia requires both cinchona and red cinchona to yield not less than 5 per cent. of total alkaloids when assayed by the foregoing process.

II.—For Quinine.

Transfer 50 c.c. of the clear filtrate remaining over from the preceding process (and representing 5 gm. of cinchona) to a beaker, evaporate it to dryness, and proceed as directed in the assay for total alkaloids, using, however, only one-half the amounts of volumetric acid and alkali there directed. Add the united chloroformic extracts containing the alkaloids in solution, gradually, and in small portions at a time, to about 5 gm. of powdered glass contained in a porcelain capsule placed over a water-bath, so that, when the contents of the capsule are dry, all or nearly all of the dry alkaloids shall be in intimate admixture with the powdered glass, and the chloroform be completely expelled.

Now moisten the residue with ether, and, having placed a funnel containing a filter of a diameter of 7 cm., and well wetted with ether, over a small graduated tube (A), transfer to the filter the ether-moistened resi-

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intended that 20 grammes of the original sample be taken and then dried to a constant weight at 100°.

The expulsion of the moisture is done to prevent an increase of the measured quantity of the solvent which is applied to the drug, and of which fractional parts, measured as closely as practicable, are afterwards taken for the extraction of the alkaloids.

The moisture which the sample contains may be inferred from the loss in weight which occurs in the drying of the sample, in case it is desired to calculate the alkaloids on the perfectly dry substance.

due from the capsule. Rinse the latter several times, if necessary, with fresh ether, so as to transfer the whole of the residue to the filter, then percolate with ether added drop by drop, until exactly 10 c.c. of percolate have been obtained. Then collect another volume of 10 c.c., by similar, slow percolation with ether, in a second graduated tube (B). Transfer the contents of the two tubes completely (using ether for washing) to two small, tared capsules, properly marked (A and B) so as to avoid confusion, evaporate to a constant weight at 100° C. (212° F.), and weigh them.

(The residue in A will contain practically all the quinine, together with a portion of the alkaloids less soluble in ether; the residue in B will consist almost entirely of these alkaloids.) From the amount of residue obtained in capsule A deduct that contained in B, and multiply the remainder by *twenty* (20). The product will represent, approximately, the percentage of *quinine* (containing 1 molecule of water) in the specimen of cinchona tested.

The United States Pharmacopœia requires cinchona to yield at least 2.5 per cent. of quinine ($C_{20}H_{24}N_2O_2.H_2O$) when assayed by the foregoing process.

As usual, the ammonia water liberates the alkaloids from their combinations in the drug, in this case from cincho-tannic and kinic acids. The mixture of alcohol and chloroform dissolves the alkaloids thus set free. By completely drying the drug at 100° C., an increase in the volume of the solvent by moisture is obviated.

The funnel should be covered, during the filtration of the liquid through the pellet of cotton, to prevent loss of solvent through evaporation.

The portions of the filtrate taken for the determination of total alkaloids and quinine are evaporated to dryness to expel alcohol and chloroform, so that the resinous matters of the filtrate may be separated by treating the residue with water; the evaporation is best done on a water-bath, the heat being kept below the boiling point of the filtrate.

The sulphuric acid acts upon the alkaloids in the residue, forming soluble sulphates with them. It is a good plan to have the water, which is added before the sulphuric acid, in a boiling condition, as the tendency of the resinous matter to form lumps may by this means be partly or completely counteracted. Normal acid volumetric solution, in known quantity, is employed to dissolve the alkaloids, so that the quantity of alkali which is required to reliberate the alkaloids may be easily judged, and conveniently used in the form of its normal volumetric solution.

In the separation and estimation of the quinine, the alkaloids are intimately mixed with powdered glass to distribute them, and thus afford the ether, which is applied to dissolve the quinine, a favorable chance to take up all of this alkaloid. The water-bath upon which the capsule containing the powdered glass is placed should be heated, but very gently; otherwise some of the contents of the capsule may be thrown out when the chloroformic washings are added. The 10 c.c. of ethereal percolate collected in tube A contain all of the quinine, and, in addition, are saturated with the other alkaloids; to find the amount of the latter with which this liquid is saturated in order that a correction in the weight of the solids in the first 10 c.c. may be made, another portion of 10 c.c. of ethereal percolate is collected and evaporated. The chloroform must be completely expelled from the powdered glass before treating the latter with ether for the removal of the quinine, or the foregoing correction for the presence of other alkaloids will not apply, since chloroform dissolves a larger quantity of these principles than ether does.

The official *Extract of Cinchona* may be assayed for total alkaloids and for quinine by treating a weighed portion (about 2 gm.) with 10 c.c. of water and 4 c.c. of normal sulphuric acid V. S., as described in the assay of the drug, and proceeding from this point exactly as directed in the place just cited. The residue of total alkaloids, after weighing, may be dissolved in chloroform, transferred to powdered glass, and treated with ether for the estimation of quinine, as in the regular assay. The results must, of course, be calculated from the quantity of extract taken.

The *Infusion of Cinchona* may be assayed by making a definite volume (200 c.c.) of it alkaline with potassium hydrate and removing the alkaloids by agitating the alkaline liquid with successive portions of chloroform in a separating funnel. The solvent is evaporated and the alkaloids weighed in the usual manner.

The *Fluid Extract*, *Tincture*, and *Compound Tincture of Cinchona* may be assayed by evaporating known volumes on a water-bath to expel alcohol, and then treating the residues as in the case of the extract. 20 c.c. of the fluid extract will suffice for a determination, and 100 c.c. of a tincture.

Assay of Iron and Quinine Citrate.

(*According to the U. S. Pharmacopœia of 1890.*)

Estimation of the Quinine.—Dissolve 1.1176 gm. of iron and quinine citrate in a capsule, with the aid of a gentle heat, in 20 c.c. of water. Transfer the solution, together with the rinsings of the capsule, to a separator, allow the liquid to become cold, then add 5 c.c. of ammonia water [to liberate the quinine from the citric acid] and 10 c.c. of chloroform, and shake. Allow the liquids to separate, draw off the chloroform layer, and shake the residuary liquid a second and a third time with 10 c.c. of chloroform. Allow the combined chloroformic extracts to evaporate spontaneously in a tared capsule, and dry the residue at a temperature of 100° to a constant weight. This residue should weigh not less than 0.1288 gm. (corresponding to at least 11.5 per cent. of dried quinine), and should conform to the reactions and tests of quinine.

Estimation of the Iron.—Heat the aqueous liquid, from which the quinine has been removed in the manner just described, on a water-bath, until the odors of chloroform and ammonia have disappeared, allow it to cool, and dilute it with water to the volume of 50 c.c. Transfer 25 c.c. of the liquid to a glass-stoppered bottle (having the capacity of about 100 c.c.), add 2 c.c. of hydrochloric acid and 1 gm. of potassium iodide, and allow the mixture to stand for half an hour at a temperature of 40°. After it has been allowed to cool, and been mixed with a few drops of starch T. S., it should require about 14.5 c.c. of decinormal sodium thiosulphate V. S. to discharge the blue or greenish color of the liquid (each c.c. of the volumetric solution indicating 1 per cent. of metallic iron).

The removal of the quinine before undertaking the estimation of the iron is rendered necessary by the fact that the alkaloid combines with iodine; hence, if this precaution is not observed, some of the iodine which is set free by the iron will be taken up by the quinine, and the quantity of iron indicated by the titration consequently appear less than the truth.

The assay of *Soluble Iron and Quinine Citrate*, for both quinine and iron, is done by the foregoing methods. The requirements for this salt are the same as for the plain citrate.

Assay of Extract of Nux Vomica.

(*According to the U. S. Pharmacopœia of 1890.*)

Extract of Nux Vomica,* *two grammes*	2 gm.
Alcohol,	
Ammonia Water,	
Water,	
Chloroform,	
Decinormal Sulphuric Acid V. S.,	
Centinormal Potassium Hydrate V. S., each, *a sufficient quantity.*	

Put 2 gm. of the dried extract of nux vomica into a glass separator, add to it 20 c.c. of a previously prepared mixture of 2 volumes of alcohol, 1 volume of ammonia water (specific gravity 0.960), and 1 volume of water, and shake the well-stoppered separator until the extract is dissolved. Then add 20 c.c. of chloroform and agitate during five minutes. Allow the chloroform to separate, remove it as far as possible, pour into the separator a few cubic centimeters of chloroform, and, without shaking, draw this off through the stop-cock to wash the outlet-tube. Repeat the extraction with two further portions of chloroform of 15 c.c. each, and wash the outlet-tube each time as just directed. Collect all the chloroformic solutions in a wide beaker, expose the latter to a gentle heat, on a water-bath, until the chloroform and ammonia are completely dissipated, add to the residue 10 c.c. of decinormal sulphuric acid, measured with great care from a burette, stir gently, and then add 20 c.c. of hot water. When solution has taken place, add 2 c.c. of Brazil wood T. S., and then carefully run in centinormal potassium hydrate V. S., until a permanent pinkish color is produced by the action of a slight excess of alkali upon the Brazil wood indicator. Divide the number of cubic centimeters of centinormal potassium hydrate V. S. used by 10, subtract the number found from 10 (the 10 c.c. of decinormal acid used), multiply the remainder by 0.0364, and that product by 50 (or multiply at once by 1.82), which will give the percentage of *total alkaloids* in the extract of nux vomica, it being assumed that strychnine and brucine are present in equal proportion, and the above factor being found by taking the mean of their respective molecular weights rounded off to whole numbers [(334 + 394) ÷ 2 = 364].

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* The words, *extract of nux vomica, dried at 100° C., two grammes*, which are given at this point in the Pharmacopœia, do not mean that, in the examination of a commercial extract, a portion of the sample is to be dried at 100° C., and that the amount specified in the assay is to be weighed off from such dried material. These words are intended to express the requirements of the Pharmacopœia that an extract of nux vomica, to be official, must be perfectly dry, and must in that condition contain 15 per cent. of total alkaloids. If it is desired to find the amount of total alkaloids which an extract containing moisture would represent if completely dried, an estimation of its moisture is made by drying at 100°, and the quantity of total alkaloids then calculated, from the percentage found by assay of the original sample, according to the methods described on page 205.

The ammonia liberates the alkaloids from the acid with which they are combined in the extract; this is either the so-called igasuric acid of nux vomica or the acetic acid used in making the extract. The free alkaloids dissolve in the chloroform and are obtained upon the evaporation of this solvent. After the chloroform has been completely dissipated by a gentle heat on the water-bath, the alkaloidal residue should be thoroughly dried, by bringing the bath to boiling, in order that every trace of ammonia may be expelled, and the possibility of small quantities of this alkali remaining, and, consequently, vitiating the result by neutralizing some of the volumetric acid solution used in titrating the alkaloids, thereby precluded. The end reaction of the titration may be more easily determined by placing near the beaker containing the solution of the alkaloids in the decinormal sulphuric acid V. S., for comparison of color, a beaker containing weak alkali solution tinted with Brazil wood test-solution, and another containing weak acid solution tinted with the same indicator.

The reactions between the alkaloids and the sulphuric acid are as follows:

$$2C_{21}H_{22}N_2O_2 + H_2SO_4 = (C_{21}H_{22}N_2O_2)_2H_2SO_4.$$
$$2C_{23}H_{26}N_2O_4 + H_2SO_4 = (C_{23}H_{26}N_2O_4)_2H_2SO_4.$$

Extract of nux vomica, when assayed by the foregoing process, should be found to contain 15 per cent. of total alkaloids.

When *Tincture of Nux Vomica* is to be assayed, 100 c.c. of it (representing 2 gm. of extract) should be evaporated to dryness on a water-bath, and the residue tested by the foregoing process. This volume of the preparation should then be found to contain 0.3 gm. of alkaloids.

Fluid Extract of Nux Vomica may be assayed by evaporating 20 c.c. of it to dryness on a water-bath, and then proceeding as in the case of the solid extract. 100 c.c. of the fluid extract should contain 1.5 gm. of total alkaloids.

The quality of *Nux Vomica* itself may be judged by preparing an extract or fluid extract from the powdered drug, according to the directions of the United States Pharmacopœia, and then assaying the product in the usual manner.

Assay of Iron and Strychnine Citrate.

(*According to the U. S. Pharmacopœia of 1890.*)

Estimation of the Strychnine.—Dissolve 2.2352 gm. of iron and strychnine citrate, in a separator, in 15 c.c. of water, add 5 c.c. of ammonia water [to liberate the strychnine from the citric acid] and 10 c.c. of chloroform, and shake. Allow the liquids to separate, draw off the chloroform layer, and shake the residuary liquid a second and a third time with 10 c.c. of chloroform. Allow the combined chloroformic extracts to evaporate spontaneously in a tared capsule, and dry the residue at a temperature of 100° to a constant weight. This residue should weigh not less than 0.02 gm. nor more than 0.02235 gm. (corresponding to not less than 0.9 nor more than 1 per cent. of strychnine), and should respond to the reactions and tests of strychnine.

Estimation of the Iron.—Heat the aqueous liquid, from which the strychnine has been removed in the manner just described, on a water-bath, until the odors of chloroform and ammonia have disappeared, allow it to cool, and dilute it with water to the volume of 100 c.c. Transfer 25 c.c. of the liquid to a glass-stoppered bottle (having the capacity of about 100 c.c.), add 2 c.c. of hydrochloric acid and 1 gm. of potassium iodide, and allow the mixture to stand for half an hour, at a temperature of 40°. After it has been allowed to cool, and been mixed with a few drops of starch T. S., it should require about 16 c.c. of decinormal sodium thiosulphate V. S. to discharge the blue or greenish color of the liquid (each c.c. of the volumetric solution indicating 1 per cent. of metallic iron).

The strychnine combines with iodine, and must be removed to prevent its interference with the estimation of the iron. Compare the action of quinine as stated on page 224.

ASSAY OF CANTHARIDES.

(*According to Baudin.*)

The value of cantharides for medicinal uses and for pharmaceutical preparations depends upon the amount of free cantharidin present. This may be conveniently estimated as follows: 25 grammes of finely powdered cantharides are put into a flask containing 100 c.c. of chloroform; the flask is stoppered, allowed to stand overnight, and then frequently shaken during the course of two or three hours. The contents are then poured upon a filter, placed in a funnel, which may be covered with a glass plate to prevent evaporation of the chloroform. 60 c.c. of the filtrate, representing the free cantharidin from 15 grammes of the drug, are collected. This liquid is evaporated in a porcelain capsule on a water-bath until the odor of chloroform is no longer perceptible. The green residue is then treated with 5 c.c. of carbon disulphide, to remove fat and coloring matter, and, by means of this liquid, transferred to a balanced filter; the insoluble portion is there washed with 10 c.c. of carbon disulphide, applied in small quantities. The filter and its contents are then transferred to an air-bath, dried for a few minutes at 60°, and weighed. 0.010 gramme is added to the weight of the cantharidin found as a correction for the solvent action of 15 c.c. of carbon disulphide on the principle. The percentage of free cantharidin is then calculated.

To determine the combined cantharidin, treat the residue from the foregoing process, in the same manner, with chloroform containing two per cent. of hydrochloric acid.

ASSAY OF DRUGS FOR FATS AND FIXED OILS.

The seed drugs and other substances yielding fats and fixed oils may usually be assayed by extraction with carbon disulphide, subsequent recovering of this solvent and weighing of the residue. The process is conveniently conducted as follows. A weighed quantity of the ground material is placed in a Soxhlet tube, or other form of continuous extraction apparatus, into which a plug of oil-free cotton has been put; the upper end of this apparatus is then attached to a reflux condenser, and the lower end connected, by means of a cork, to a weighed flask containing a convenient quantity of carbon disulphide. Heat is applied to the flask by means of a water-bath, and the process of percolation continued for several hours. The heat is then withdrawn, the flask containing the oil and solvent detached from the apparatus and connected with an ordinary condenser; the solvent is then distilled off by the heat of a water-bath, and the contents of the flask heated on the bath until they cease to lose weight. By deducting the weight of the flask from that of the flask and oil, the weight of the last, in the quantity of original material taken, is found. The United States Pharmacopœia requires *ground linseed*, when extracted with carbon disulphide, to yield not less than 25 per cent. of fixed oil.

ASSAY OF DRUGS FOR RESINS.

The estimation of the resinous matter in a drug is accomplished by exhausting a weighed portion of the powdered material with alcohol or ether, concentrating the solution of the resin to a small bulk, pouring it into cold water contained in a weighed beaker, retaining the precipitate in the beaker or collecting it upon balanced filters, washing it with water, drying it at 100°, and weighing it. When alcohol is used as the solvent, the extraction may be done by simple percolation; when ether is employed to remove the resin from the drug, continuous extraction as directed on this page for the estimation of fixed oil may be conveniently used. The United States Pharmacopœia gives the following requirements for *jalap*: "On exhausting 100 parts of jalap with alcohol, concentrating the tincture to 40 parts, and pouring it into water, a precipitate of resin should be obtained, which, when washed with water, and dried, should weigh not less than 12 parts, and of which not over 10 per cent. should be soluble in ether." *Scammony*, *podophyllum*, and other resinous drugs may be assayed in a similar manner. *Tinctures* and *fluid extracts of resinous drugs* are concentrated by evaporation, and then precipitated with water, in the manner described.

ASSAY OF DRUGS AND OTHER MATERIALS FOR TANNINS.

The estimation of tannin in the official astringent drugs may be accomplished by what is known as the hide-powder method of assay. For this purpose, an infusion is made by heating from 10 to 20 gm. of the ground material with 200 c.c. of water in a beaker placed in a boiling water-bath for one-half hour. The clear liquid is then poured into a liter flask, and the extraction repeated with 200 c.c. of water at a time, until one liter of infusion is obtained. This infusion is allowed to become cold, its volume then adjusted to the mark by adding water, and thoroughly mixed by shaking. A portion of it is then percolated through hide powder to remove the tannin from solution ; by evaporating portions of the infusion before and after this percolation, and subtracting, the difference will indicate approximately the amount of tannin present,—at all events, it will give the best idea of the astringency of the drug, or the true value of the material for tanning purposes. The operation is conducted as follows. A small glass percolator, about 18 cm. in total length and about 2.5 cm. in diameter at its wide end, is fitted with a loose plug of absorbent cotton, pushed lightly down to the shoulder. Hide powder is then loosely dropped in, with moderate shaking, until the percolator is filled to within about 3 cm. of the top. Another plug of absorbent cotton is then placed in the open end sufficiently firmly to support the powder when the percolator is inverted. The neck of the latter is then connected with a rubber tube of sufficient length to permit it being used as the long arm of a siphon. The percolator is then inverted in a wide-mouthed bottle. The rubber tube is run up through a clamp or retort ring so as to give it a good curve, thus preventing it from bending and stopping the flow of liquid, and thence into a graduated cylinder. The infusion is next poured into the bottle, a little at a time, in order to moisten the hide powder by capillary attraction rather than by pressure. When the bottle and percolator are both filled, suction is applied to the open end of the rubber tubing very gradually, so as not to cause the hide powder to pack. As soon as sufficient liquid has been drawn into the tube to cause the latter to act as a siphon, the open end is lowered into the cylinder. The first 30 or 40 c.c. of liquid that pass through are liable to contain some soluble matter of the hide powder. This portion should therefore be tested with a solution of tannic acid in water, and, if a precipitate is produced, rejected. If the addition of tannic acid to the liquid causes no precipitate, it is advisable to test another portion of the liquid with a solution of gelatin, to make sure that the detannation of the infusion has been complete. If the liquid does not precipitate with either of these tests, the next 50 c.c. of it that pass through are collected in the cylinder, transferred to a weighed dish, or beaker, and evaporated to constant weight on a water-bath. By evaporating in the same manner 50 c.c. of the filtered original infusion, the difference in the weight of the residues will give the amount of tannin in 50 c.c. of the infusion. The percentage amount is then calculated from this difference and the quantity of drug represented by 50 c.c. of the infusion.

In place of the given weight of drug, the corresponding volume in cubic centimeters of an *astringent fluid extract*, or about the fifth part in weight of an *astringent solid extract*, is to be taken. Ten or twenty times as much of an *astringent tincture* as of fluid extract is taken for an estimation. Fluid extracts and tinctures are evaporated to expel alcohol, and the solid extracts obtained in this manner, as well as originally solid extracts, are treated with warm water, and the infusions made up to a liter. These infusions are allowed to cool, then filtered, and tested in the manner already described for those of crude drugs.

ASSAY OF EXTRACT OF LICORICE.

The United States Pharmacopœia states that not less than 60 per cent. of a commercial extract of licorice should be soluble in cold water; it gives no method of estimating the quantity of glycyrrhizin present. The following process has been adopted, for the analysis of the commercial extract, or licorice mass, by the large consumers and manufacturers in the United States.

"*Moisture.*—Expose about two grammes of the mass in a platinum or porcelain crucible in a water-oven until hardened. Then divide the dry residue in small pieces with a penknife; heat again until the weight is constant.

"*Mineral Matter.*—Place the same crucible, with mass as above, over a Bunsen burner until the ashes are white.

"*Insoluble Substance.*—Dissolve 5 gm. of the mass in 100 c.c. of distilled water (100° C.) and decant, after twelve hours, the supernatant solution from the sediment through a dried and weighed filter, also collect sediment on same by using cold water in rinsing the beaker. A further sediment is noticed in the filtrate after another twelve hours' subsidence, because traces of starch unavoidably pass through the filter, which is treated as above and collected on a second filter. These two quantities shall be the insoluble substance.

"*Gummy Matter.*—Dissolve 5 gm. of the mass in a beaker with 50 c.c. of distilled water (100° C.). When completely dissolved, pour in 100 c.c. of alcohol (95 per cent.), and vigorously stir. Allow to subside overnight, filter the precipitate on a dried and weighed filter, and wash the residue with a mixture of two parts alcohol (95 per cent.) and 1 part of water until the filtrate passes colorless. By drying the residue in a water-oven and weighing, the combined percentages of insoluble substance and gummy matter are obtained. On deducting the percentage of the insoluble substance from this, the percentage of gummy matter is determined.

"*Glycyrrhizin.*—Concentrate the alcoholic filtrate from the foregoing residue (insoluble substance and gummy matter) to the volume of 30 c.c. and transfer to a tared beaker by using about 20 c.c. of water. Add 12 drops of sulphuric acid previously diluted with 5 c.c. of water, while stirring, to precipitate the glycyrrhizin, and set aside overnight in a cool place. Pour off the liquid through a filter and wash the glycyrrhizin three times with ice-cold water by decanting. One drop of concentrated ammonia water is added to neutralize any acid remaining. The drying is carried out in a water-oven to constant weight.

"*Saccharine Matter.*—The liquid decanted from the precipitated glycyrrhizin is neutralized with barium hydrate, and the formed barium sulphate separated by filtration. The amount of saccharine matter in the filtrate is determined with Fehling's solution.

"*Extractive Substance.*—The balance which remains by adding the percentages of water, mineral matter, insoluble substance, gummy matter, glycyrrhizin, and saccharine matter, and subtracting the amount from 100, gives the amount of extractive substance."

Fluid extract of licorice, the official *pure extract of licorice* and *ammoniated glycyrrhizin*, may be examined for their glycyrrhizin according to the general outlines of this method.

VALUATION OF CARBOLIC ACID.

The following method is that of the United States Pharmacopœia:

"Dissolve 1.563 gm. of the carbolic acid to be valued in a sufficient quantity of water to make 1000 c.c. Transfer 25 c.c. of this solution (containing 0.039 gm. of the acid) to a glass-stoppered bottle having a capacity of about 200 c.c., add 30 c.c. of decinormal bromine volumetric solution (which is 5 c.c. more than would be required if the carbolic acid in the solution were absolute phenol, the excess being added to promote the formation and separation of tribrom-phenol), then 5 c.c. of hydrochloric acid, and immediately insert the stopper. Shake the bottle repeatedly in the course of half an hour, then remove the stopper just sufficiently to introduce quickly 5 c.c. of a 20-per-cent. aqueous solution of potassium iodide, being careful that no bromine vapor escape, and immediately stopper the bottle. Shake the latter thoroughly, remove the stopper and rinse it and the neck of the bottle with a little water, so that the washings may flow into the bottle, and then add, from a burette, decinormal sodium thiosulphate volumetric solution until the iodine tint is exactly discharged, using towards the end a few drops of starch test-solution as indicator. Note the number of cubic centimeters of decinormal sodium thiosulphate volumetric solution consumed. Deduct this from 30 (the number of cubic centimeters of decinormal bromine volumetric solution originally added), and multiply the remainder by 4. The product will, approximately, represent the percentage of absolute phenol in the carbolic acid tested."

The formation of tribrom-phenol in the foregoing estimation takes place in accordance with the equation—

$$C_6H_5OH + 3Br_2 = C_6H_2Br_3OH + 3HBr.$$

Any tribrom-phenol bromide which is precipitated with the tribrom-phenol decomposes potassium iodide in the presence of free hydrochloric acid, with the liberation of iodine and the formation of tribrom-phenol, as follows:

$$2KI + C_6H_2Br_3OBr + HCl = I_2 + KBr + KCl + C_6H_2Br_3OH.$$

The two atoms of iodine which are thus set free represent two atoms of bromine, which, in the absence of potassium iodide, would be absorbed and, accordingly, make the result too high.

All the other reactions which occur in this process are fully described under the consideration of decinormal bromine volumetric solution.

VALUATION OF PEPSIN.

The methods of valuing pepsin are, at best, only comparative tests. They must be carried out under the same conditions, for it has been found that slight variations in the process and quantities of the materials will cause very different results to be obtained, even with the same pepsin.

The United States Pharmacopœia requires pepsin to be capable of digesting not less than 3000 times its own weight of freshly coagulated and disintegrated egg albumen, when tested by the official process, which is as follows:

"Prepare, first, the following three solutions:

"*A*. To 294 c.c. of water add 6 c.c. of diluted hydrochloric acid.

"*B*. In 100 c.c. of solution *A* dissolve 0.067 gm. of the pepsin to be tested.

"*C*. To 95 c.c. of solution *A*, brought to a temperature of 40° C., add 5 c.c. of solution *B*.

"The resulting 100 c.c. of liquid will contain 2 c.c. of diluted hydrochloric acid, 0.00335 gm. of the pepsin to be tested, and 98 c.c. of water.

"Immerse and keep a fresh hen's egg during fifteen minutes in boiling water; then remove it and place it into cold water. When it is cold, separate the white, coagulated albumen, and rub it through a clean sieve having 30 meshes to the linear inch. Reject the first portion passing through the sieve. Weigh off 10 gm. of the second, cleaner portion, place it in a flask of the capacity of about 200 c.c., then add one-half of solution *C*, and shake well, so as to distribute the coherent albumen evenly throughout the liquid. Then add the second half of solution *C*, and shake again, guarding against loss. Place the flask in a water-bath, or thermostat, kept at a temperature of 38° to 40° C., for six hours, and shake it gently every fifteen minutes. At the expiration of this time the albumen should have disappeared, leaving at most only a few, thin, insoluble flakes. (Trustworthy results, particularly in comparative trials, will be obtained only if the temperature be strictly maintained between the prescribed limits, and if the contents of the flasks be agitated uniformly, and in equal intervals of time.)

"The relative proteolytic power of pepsin stronger or weaker than that described above may be determined by ascertaining, through repeated trials, how much of solution *B* made up to 100 c.c. with solution *A* will be required exactly to dissolve 10 gm. of coagulated and disintegrated albumen under the conditions given above."

For an account of the digestive action on proteids, see page 788, Volume I.

Saccharated pepsin, when tested by the foregoing process, with the modification that 0.67 gm. of it are to be taken in preparing solution *B*, should digest 300 times its own weight of freshly coagulated and disintegrated egg albumen, according to the requirements of the United States Pharmacopœia.

The proteolytic power of the various *liquid* and *solid preparations of pepsin* may be determined by following the general outlines of the foregoing process:

VALUATION OF PANCREATIN.

Pancreatin digests albuminoids and converts starch into sugar. Prolonged contact with mineral acids renders it inert; its activity is determined in an alkaline medium. The United States Pharmacopœia prescribes the following method for its valuation:

"If there be added to 100 c.c. of tepid water contained in a flask, 0.28 gm. of pancreatin and 1.5 gm. of sodium bicarbonate, and afterwards 400 c.c. of fresh cow's milk previously heated to 38° C., and if this mixture be maintained at the same temperature for thirty minutes, the milk should be so completely peptonized that, if a small portion of it be transferred to a test-tube and mixed with some nitric acid, no coagulation should occur."

According to E. G. Eberhardt, the end of the reaction seems to be reached when diluted nitric acid produces only a finely granular precipitate that does not separate as a curd. R. H. Jones heats the mixture to 52.5° C. until it responds to the official test. Both of these authorities suggest that the digestive power of the sample on starch be ascertained. For the manner of doing this, see the valuation of diastase given below.

It is obvious that the relative peptonizing power of pancreatin stronger or weaker than that described above may be determined by ascertaining, through repeated trials, how much of the sample will be required to completely peptonize 400 c.c. of milk according to the foregoing process.

VALUATION OF DIASTASE AND DIASTASIC SUBSTANCES.

The following elaboration of Jungk's method of testing diastasic digestants has been proposed, chiefly by J. M. Francis. It includes both the starch-liquefying and the starch-saccharifying action of the diastase. It may also be used to determine the power of pancreatin, and of the ptyalin of saliva on starch.

Solution of Digestant.—Weigh out 5 grammes (or any desired amount) of the malt extract or other substance to be tested, and dissolve it in enough water to make 100 c.c. of solution; in the case of powerful digestants use a smaller quantity. If the substance be a solid, it should be taken in the form of a very fine powder. If a portion of the substance is not readily soluble, or is insoluble in water, allow maceration with this liquid in a warm place for one-half hour, then filter off any insoluble matter, wash the same, collect the washings with the filtrate, and adjust the volume of the clear solution at the ordinary temperature; in some cases it may be advisable to apply the water in two portions. If the diastasic substance is already in solution, and it is desired to find the digestive strength by volume instead of by weight, it is simply necessary to measure out the portions required in the test.

Iodine Solution.—Prepare a solution by dissolving 2 gm. of iodine in

200 c.c. of distilled water containing 5 gm. of potassium iodide; adjust to 250 c.c. This solution should be kept in a dark place, and be made up fresh every two months.

Iodine Dilution.—Add 1.5 c.c. of the foregoing iodine solution to a sufficient quantity of distilled water to produce 1000 c.c., and mix well. This dilution should be prepared immediately before use, as it is very delicate. For use, fill a dozen clear, two-ounce vials with the dilution, and arrange them, side by side, in a row, upon a sheet of white paper.

Starch Solution.—Into a counterpoised beaker or other container of sufficient size pour about 400 gm. of distilled water; bring this water to violent ebullition before adding the starch. In the mean time weigh out 10 gm. of neutral potato starch (previously dried at 100° C.), transfer it to a beaker, add about 50 c.c. of cold, distilled water, and stir until a smooth cream results. Pour this mixture of starch and water into the boiling water, stirring the latter constantly during the pouring with a weighed, rubber-tipped glass rod. Rinse out the remaining traces of starch from the beaker, add them to the paste, and stir the latter till a smooth, homogeneous product is obtained; allow this to boil vigorously for fifteen minutes; transfer beaker and contents, including stirring-rod, to a balance, add sufficient distilled water to make the paste weigh 500 gm., then stir it to thoroughly incorporate the water and make a uniform mixture. If the product contains any lumps it must be rejected and a fresh lot prepared.

Performing the Test.—Counterpoise a wide-mouthed bottle and pour into it 100 grammes of the starch paste. Transfer the bottle, with its contents, to a water-bath kept at a temperature of 40° C., and allow it to remain until the paste attains the temperature of the bath. Then remove the bottle, add to the paste a quantity of the digestant solution supposed to be sufficient to cause complete digestion in the specified time, shake the mixture vigorously, and replace the bottle and contents in the water-bath, maintaining the heat of the latter at 40° C. After one minute, by means of a minim dropper, remove two minims of the mixture from the bottle, and add them to a vial of the iodine dilution; observe the effect, and repeat the test, at intervals of one minute, until *no change* of tint is produced in a vial of the dilution standing on a white base and between two other vials of the dilution to which no starch solution has been added. Note the time required to reach this point. The knowledge sought through the test is either the time required to digest a specified amount of starch or the amount of starch digested in a specified period of time. The latter specification is deemed the better. And the limit of time has been placed at thirty minutes, because this is the interval during which a diastase will act; or, in other words, under ordinary circumstances half an hour will elapse after the ingestion of a meal before the normal increase of acid secreted in the stomach will be sufficient to inhibit the further action of the diastase. If, therefore, in the test, the digestion is completed in less than thirty minutes, repeat the test, employing a proportionately smaller measure of the digestant solution, until the proportion required to digest 100 gm. of the starch paste in thirty minutes is determined. If desired, several tests may be undertaken at once, or any other specified period of time may be employed in the test.

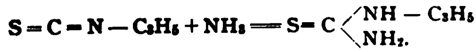
To find the number of parts of starch which one part of the diastasic substance will digest under the specified conditions, divide the weight of starch (2 gm.) contained in 100 c.c. of the paste by the weight of the digestant represented by the volume of the solution of the latter which was used.

VALUATION OF VOLATILE OIL OF MUSTARD.

The United States Pharmacopœia gives the following method for determining volatile oil of mustard:

"If a mixture of 3 gm. of the oil and 3 gm. of alcohol be shaken, in a small flask, with 6 gm. of ammonia water, it will become clear after standing for some hours, or rapidly when warmed to 50° C., and usually deposit, without becoming colored, crystals of thiosinamine (allyl-thiourea, $CS.N_2H_3(C_3H_5)$)."

The allyl isosulphocyanate of the oil of mustard and the ammonia gas react as follows:



$$S=C=N-C_3H_5+NH_3=S=C\begin{cases}NH-C_3H_5\\NH_2.\end{cases}$$

The alcohol takes no part in the reaction; it is used simply to dissolve the oil, and by this means bring the latter into closer contact with the ammonia of the aqueous solution.

"To determine the proportion of thiosinamine obtainable from the oil, decant the mother-water from the crystals, and evaporate it gradually in a tared capsule, on a water-bath, adding fresh portions only after the ammoniacal odor of each preceding portion has disappeared. Then add the crystals from the flask to those in the capsule, rinsing them out of the flask with a little alcohol, and heat the capsule on a water-bath until its weight remains constant. The amount of thiosinamine thus obtained from 3 gm. of the oil should be not less than 3.25 gm., nor more than 3.5 gm. After cooling, thiosinamine forms a brownish, crystalline mass, fusing at 70° C., and having a leek-like, but no pungent, odor. The mass should be soluble in 2 parts of warm water, forming a solution which should not redden blue litmus paper, and which possesses a somewhat bitter, not persistent taste."

ASSAY OF FORMALDEHYDE.

A simple and rapid, as well as reasonably accurate, method of assaying the commercial products of formaldehyde is that proposed by Carl E. Smith; it is a modification of the ammonia method first proposed by Legler, which is based on the fact that free ammonia and formaldehyde react to form hexamethylene-tetramine.

The process is conducted as follows. Dissolve 2 gm. of pure neutral ammonium chloride in 25 c.c. of water and introduce it into a flask provided with a well-fitting stopper. Add 2.25 gm. of the sample of formaldehyde, and then run in from a burette 25 c.c. of normal potassium or sodium hydrate volumetric solution. Stopper the flask at once and put it aside for one-half hour. Then add a few drops of rosolic acid test-solution, and determine the excess of ammonia with normal sulphuric acid volumetric solution; each cubic centimeter of normal potassium hydrate consumed indicates 2.0 per cent. of formaldehyde.

The reactions involved are as follows:

$$NH_4Cl + KOH = NH_4OH + KCl;$$

then,

$$6CH_2O + 4NH_4OH = N_4(CH_2)_6 + 10H_2O.$$

The ammonia combines with the formaldehyde nearly as fast as it is liberated, and, consequently, has little chance to volatilize.

The presence of commercial methyl alcohol appears to lower the result slightly, while pure methyl alcohol and acetone exert, practically, no influence.

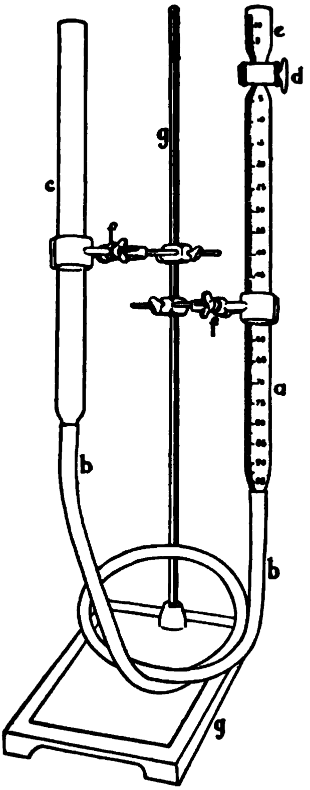
Many chemists have found it necessary to allow the ammonia and formaldehyde more time in which to react; and L. F. Kebler recommends six hours as the minimum period.

CHAPTER II.

GASOMETRIC ESTIMATIONS OF THE UNITED STATES PHARMACOPŒIA.

THE United States Pharmacopœia directs the strengths of the official nitrites to be determined by measuring the volume of nitrogen dioxide given off during a definite reaction. The volume of this gas is to be determined by causing the reaction to take place in a nitrometer. The construction of this instrument is shown in Fig. 13. It consists of a measuring tube, *a* (graduated in tenth cubic centimeters), provided with the stop-cock, *d*, and the graduated funnel tube, *e*, and connected by stout rubber tubing, *b*, with an open equilibrium tube, *c;* these tubes are attached to a stand, *g g*, by suitable clamps, *f f*, in such a manner that either tube may be readily and quickly clamped at a higher or lower level.

FIG. 13.



The Pharmacopœia directs the estimation to be performed as follows: "The stop-cock of the measuring tube having been opened, and the open equilibrium tube having been raised to a higher level, pour into the latter a saturated aqueous solution of sodium chloride, until the measuring tube, including the bore of the stop-cock, is completely filled. Then close the latter and fix the equilibrium tube at a low level. Having ascertained that the stop-cock is closed air-tight, and having, if necessary, wiped out the graduated funnel tube, *e*, introduce into it the prescribed quantity of the liquid to be tested, and allow this to flow slowly into the measuring tube, being careful not to admit any air. Follow it by the prescribed quantities of the several reagents (potassium iodide test-solution and normal sulphuric acid volumetric solution). When the reaction, which takes place at once, moderates, remove the measuring tube from its clamp, and, being careful to hold it constantly so that the liquid contained in it stands at a higher level than that in the equilibrium tube, shake its contents, without permitting any gas to pass into the open tube. When the reaction has completely ceased, restore the tube to its fastening, and allow the apparatus and contents to acquire the ordinary temperature of the room, which is assumed to be at or about 25° C. (77° F.). Then adjust the two tubes so that the liquid columns are at exactly the same level, and read off the volume of gas in the measuring tube. Multiply this figure by the weight of the substance yielding 1 c.c. of nitrogen dioxide [see page 238]. The result will be the weight of the pure nitrite contained in the amount of the sample taken for the assay."

The reactions which take place in these estimations may be conveniently illustrated by the following example, in which B stands for a univalent base, either organic or inorganic. The sulphuric acid first decomposes the nitrite with the liberation of nitrous acid and the formation of a sulphate,—

$$2BNO_2 + H_2SO_4 = B_2SO_4 + 2HNO_2.$$

The potassium iodide then decomposes the nitrous acid with the evolution of nitrogen dioxide, according to the equation :

$$2KI + 2HNO_2 = H_2O + K_2O + I_2 + N_2O_2.$$

The excess of sulphuric acid at once converts the potassium oxide into potassium sulphate ; it and the other sulphate usually remain dissolved in the brine. The iodine which is liberated colors the solution in the nitrometer, and sometimes separates as a blackish solid.

The Pharmacopœia states that the determination will be sufficiently exact for pharmacopœial purposes if the evolved gas be measured at the ordinary in-door temperature previously referred to ; barometric pressure is assumed to be normal, and the tension of aqueous vapor is disregarded.

At 25° C. (77° F.), and 760 mm. pressure, one cubic centimeter of nitrogen dioxide is the equivalent of:

	Gramme.
Nitrogen Dioxide, NO	0.0012297 *
Amyl Nitrite, $C_5H_{11}NO_2$	0.0047923
Ethyl Nitrite, $C_2H_5NO_2$	0.0030716
Sodium Nitrite, $NaNO_2$	0.0028283

The following articles are those directed to be tested gasometrically, according to the foregoing method, by the United States Pharmacopœia; the quantities stated are those prescribed by this authority:

Amyl Nitrite.—"If 0.26 gm. of amyl nitrite, diluted with about 5 c.c. of alcohol, be introduced into a nitrometer, followed by 10 c.c. of potassium iodide T. S., and afterwards by 10 c.c. of normal sulphuric acid V. S., the volume of nitrogen dioxide generated, measured at the ordinary in-door temperature, should be about 40 c.c. (each c.c. indicating about 2 per cent. of pure amyl nitrite)."

Sodium Nitrite.—"If 0.15 gm. of sodium nitrite be dissolved in 5 c.c. of water, and introduced into a nitrometer, then followed by a solution of 1 gm. of potassium iodide in 6 c.c. of water and 15 c.c. of normal sulphuric acid V. S., the liberated nitrogen dioxide should measure not less than 51.7 c.c. at 25° C., corresponding to not less than 97.6 per cent. of the pure salt."

Spirit of Nitrous Ether.—This is an alcoholic solution of ethyl nitrite, $C_2H_5NO_2$.

"If 5 c.c. of recently prepared spirit of nitrous ether be introduced into a nitrometer, and followed, first, by 10 c.c. of potassium iodide T. S., and then by 10 c.c. of normal sulphuric acid, the volume of nitrogen dioxide generated at the ordinary in-door temperature should not be less than 55 c.c. (corresponding to about 4 per cent. of pure ethyl nitrite)."

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[*] One liter of nitrogen dioxide weighs, at 0° C. and 760 mm., 1.3423 gm.; and, at 25° C. and 760 mm., 1.2297 gm.

CHAPTER III.

DETERMINATION OF SOME PHYSICAL CONSTANTS.

THIS section is devoted to the description of some of the special methods of examination by which the United States Pharmacopœia seeks to distinguish one substance from another, to fully identify it, or to prove its purity.

DETERMINATION OF SPECIFIC GRAVITY.

The specific gravity of most liquids can be determined by means of the hydrometer, which is simply floated in the liquid, and the point to which it sinks noted. The specific gravity is then either read directly on a scale which is made upon the stem of the instrument, or it is found by reference to a table from a figure on the stem. A very convenient method of taking specific gravity is by means of the Westphal balance. This apparatus and the manner of using it are fully described on page 35 of Volume I. The specific gravities of liquids are generally ascertained, however, by the use of a specific gravity bottle or pyknometer. This is an instrument which can readily be constructed by the operator as follows. A flask of convenient size, say capable of holding 25 c.c., and having a narrow neck, is thoroughly cleaned and dried. Two file-scratches are then made across the neck of the flask, about an inch below the mouth; the scratches should be parallel to each other, and should be sufficiently distant to mark the upper and lower points of the meniscus when the flask is filled to the upper mark with liquid. The dry flask is then accurately weighed. It is next filled with distilled water, which has been recently boiled, to exclude air, and allowed to cool out of contact with air. The flask with its contents is then set in a bath of water, whose temperature is decidedly below that desired for the standardization of the specific gravity bottle. A thermometer is kept in the bath, and when the temperature has risen to the desired point, the meniscus of the water in the flask is adjusted between the two file-marks by introducing more of the liquid or removing some by means of filter paper, as the case requires. When the volume of water has been so adjusted, and the proper temperature attained, the flask is removed from the bath, thoroughly wiped dry on the outside, and accurately weighed together with the contained water. The weight of the dry empty flask deducted from the weight of the flask and water leaves the weight of the volume of water which the flask holds to the mark at the particular temperature employed. Owing to the fact that glassware contracts for a year or two after it is blown, all specific gravity bottles should be accurately tested, from time to time, with water, in order to prove that they are correctly graduated. Whenever specific gravity is mentioned in the United States Pharmacopœia, without a given temperature, it is to be understood to refer to a temperature of 15° C. as compared with water at the same temperature; for this reason the specific gravity bottle should be standardized at 15° C. When the specific gravity of a liquid is given, it is necessary to state not only the temperature of the liquid, but also that of the standard (water) with which it is compared. These two values are now usually given in the form of a fraction, the numerator of which represents the temperature of the liquid in question, while the denominator represents the temperature of the standard. Thus, $\frac{25^\circ\text{ C.}}{15^\circ\text{ C.}}$ denotes that the specific gravity of the liquid is given for the temperature of 25° C., as compared with water at 15° C.

To take the specific gravity of a liquid with the bottle, see that it is perfectly clean and dry; then fill it with the liquid to a point above the mark; afterwards place it, with its contents, in a bath of cold water as described in the graduation of the bottle, and leave it there until the proper temperature is reached; then remove any excess or supply any deficiency of liquid, so that the contents shall coincide with the marks on the neck of the flask; finally remove the latter, with its contents, from the bath, wipe the outside dry, and weigh the flask and contents. From the weight of the whole deduct the weight of the flask; the difference is the weight of this volume of the liquid. To calculate the specific gravity, divide this weight by the weight of the equal volume of water.

The liquid to be examined should always be thoroughly mixed before filling the specific gravity bottle with it, since, in the event of the liquid being a mixture of several substances of different specific gravities, there may be a separation of the constituents, and the portion taken for the specific gravity determination may not be representative of the entire lot.

In taking the specific gravity of honey, the United States

Pharmacopœia directs, on account of the viscidity of this substance, that it be diluted with two parts of water. The specific gravity of the resulting liquid is then taken, and, from the figure found and the data of the dilution, the specific gravity of the original liquid is calculated.

The specific gravity of alcohol or of any mixture of alcohol and water may, however, also be ascertained by means of an accurate hydrometer, preferably that prescribed by the United States government for the use of internal revenue and custom-house officers. While 15° C. has been adopted by the United States Pharmacopœia as the temperature for taking specific gravities in general, in the case of alcohol and wine, however, the temperature of 60° F. (15.555° C.) has been retained, since all the laws and regulations of the United States, referring to alcohol and alcoholic liquids in general, are based on this degree of temperature. In taking the specific gravity of alcohols, ether, and chloroform, the temperature of 25° C. is sometimes also employed.

The specific gravities of semi-solids, such as lard and petrolatum, can be taken by melting the substance, filling the bottle with the warm liquid, adjusting the volume to the mark at 60° C., and from this point proceeding as in the regular manner. Chloral is melted at about 58° C., and the specific gravity of the resulting liquid is taken at that temperature. The Westphal balance is especially adapted for taking the specific gravities of substances which need to be melted. The taking of the specific gravities of solids is discussed on page 33, Volume I.

DETERMINATION OF SOLUBILITY.

The determination of solubility or insolubility is an important test in connection with all substances. The solvents mentioned in the United States Pharmacopœia are water, alcohol, mixtures of water and alcohol,* ether, mixtures of alcohol and ether, chloroform, glycerin, benzin, benzol, carbon disulphide, acetic ether, glacial acetic acid, fixed and volatile oils, alkali hydrates and carbonates, and mineral acids.

The estimation of the amount or degree of solubility may frequently be used as a means of identifying a substance, or of detecting a substitution. The test of solubility in glycerin, fixed and volatile oils, alkalies, and mineral acids is chiefly of qualitative character. When alkalies are used, as in the testing of the official resins, it is customary to note the effect of an excess of acid on the solution ; when strong mineral acids, as, for example, sulphuric acid, are employed as solvents, water is sometimes added to the solution to ascertain if the substance will precipitate on dilution.

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* Rules for making an alcohol of any required lower percentage from an alcohol of any given higher percentage will be found on page 317.

The solubility of a substance is frequently taken both at 15° C. and the boiling point of the solvent ; thus, in water at 15° and 100° C.

The determination of the degree of solubility of a solid is generally done by adding an excess of the substance in a powdered condition to a portion of the solvent, which has been heated in a flask to the desired temperature ; the whole is then brought to the same degree of heat, and maintained at this point, with frequent shakings, for several hours. The saturated solution so obtained is then filtered through an ashless filter paper placed in a funnel, the temperature of both paper and funnel having been brought to that of the solution. The filtrate is collected in a tared flask ; if necessary, from the liquid having been heated above the ordinary temperature, the flask is stoppered and allowed to cool with its contents. If an elevated temperature has been employed, the stopper is removed to admit air, when the ordinary temperature is attained ; in such cases, the stopper is immediately replaced and the whole weighed. The entire solution, or an aliquot part of its weight, is then evaporated on a water-bath, and the residue finally dried in an air-bath at a suitable temperature, until the weight is constant. The weight of the residue is the amount of the dissolved substance. This weight deducted from the weight of the solution evaporated leaves the weight of solvent present. Upon dividing the weight of the solvent by the weight of the dissolved substance, the quotient will express the number of parts of the solvent required to dissolve one part of the substance.

Sometimes in determining the solubility of the ordinary inorganic salts, instead of evaporating the solution and weighing the residue, the base or acid is estimated, in a definite weight of the solution, by the usual gravimetric or volumetric methods, and the quantity of the dissolved salt calculated from the result of this operation.

Great care must be taken in handling inflammable liquids in the foregoing process. In such cases it will be found advisable, during the digestion of the substance with the solvent, to attach the flask to an upright condenser, and to carefully distil off the solvent in the subsequent effort to obtain the dissolved substance for weighing.

These methods of determining solubility are, of course, inapplicable in the case of volatile solids. The approximate solubility of these substances at ordinary temperatures may be found by placing in a weighed flask, provided with a well-fitting, weighed stopper, a convenient weight of the substance, and adding the solvent in small portions, every 10 or 15 minutes, with continual agitation during the intervals, the flask being kept stoppered until complete solution is just effected. The increase in the weight of the flask and its contents, brought about by the addition of the solvent, shows the amount of the solvent used. The degree of solubility may then be calculated in the usual way.

To determine the soluble matter in a substance partly insoluble, which is frequently required to be done, as, for instance, in testing the official resins and some resinous drugs, it will be found convenient to collect the insoluble part of the substance on a weighed or balanced filter, and, after washing the filter and its contents, to dry and weigh the insoluble matter. The results obtained in this manner may be checked, except in the presence of dissolved volatile substances, by evaporating the filtrate and washings to a constant weight.

The solubility or miscibility of liquids also is determined. This is most conveniently done by taking, in a graduated cylinder, a definite volume of the liquid to be tested, and gradually adding the solvent, with thorough agitation after each successive portion, until a clear solution is obtained. The increase in volume due to the addition of the solvent is noted, and, from the respective volumes of the two liquids employed, the degree of solubility by volume of the original substance is calculated by division. This method does not take into consideration any contraction in volume that may occur, and, as a rule, this feature may be disregarded for the small quantities of liquids operated on. But, if it is desired to take this shrinkage into account, the solvent may be added from a definite volume of it contained in a graduated vessel, and, assuming no loss to have occurred by evaporation or from other cause, the volume required found by noting the bulk taken from the vessel. To obtain the data for finding the parts by weight of a solvent in which one part of a liquid is soluble, it is, of course, only necessary to weigh the portion of the original substance taken and the final solution, and deduct the first weight from the second one.

Sometimes certain liquids are said to be miscible in all proportions, which statement means that a clear solution will result no matter what be the weight or volume of the liquids added to each other.

Some complex liquids may dissolve only in part in one solvent, but completely in another. The first property is indicated by repeated additions of the solvent failing to cause a decrease in the bulk of the fluid being tested. In the case of some complex liquids, one constituent seems to exert a solvent action on another, or the liquid itself becomes the solvent, as is evidenced by the fact that the liquid yields a clear solution with a small portion of a solvent, but fails to dissolve completely in a larger quantity.

The immiscibility or insolubility of liquids in each other is indicated when, upon shaking together known volumes of the two liquids, the layers which separate exactly equal the original volumes. The test of the miscibility of a liquid is sometimes conducted by the means just mentioned, the degree of miscibility being inferred from the decrease in the bulk of the layer of the liquid under examination.

DETERMINATION OF MELTING POINTS.

A constant melting point is a characteristic property of many well-defined chemical substances, and, on that account, an investigation of this feature is often a useful means of examining the quality of substances. The melting point is the lowest degree of heat which will liquefy a solid. The determination of this constant is usually effected as follows. A small quantity of the substance is put into a capillary tube sealed at one end; this tube is then attached to the bulb of a thermometer by means of twine or a piece of platinum wire; the bulb and closed end of the capillary are then immersed in a suitable bath, and heat applied to the same with a small flame. A constant watch is kept on the contents of the tube and the mercury column, and the heat very slowly increased until liquefaction occurs; the temperature at which this takes place is noted as the melting point.

Friable substances are pulverized before being put into the tube. In the particular cases of fats and waxes a capillary tube, open at both ends, is dipped into a little of the melted specimen, and, after solidification is complete, is wiped and attached to a thermometer in the usual way. Both are then placed in a vessel of water, which is gradually heated; the temperature at which the fat, or wax, and water rise in the tube is taken as the melting point.

The walls of the capillary tube should be very thin. The bath may be composed of mercury, water, or paraffin. Mercury is used when the melting points of certain substances, which are liquid at ordinary temperatures, are to be taken. Water is employed as the bath when the substance is solid at ordinary temperatures but fusible below 100° C., while paraffin may be conveniently used between this point and the boiling point of mercury. The bath should be continuously stirred, during the whole operation, to equally distribute the heat; this matter is assisted by having the bath contained in two beakers, both partly filled, and one of them placed inside of the other.

It may happen in the operation that the solid material in the tube will shrink or become coherent; if so, the temperature at which this takes place should be recorded, as the phenomenon may have some significance. Where this behavior is liable to occur from loss of adhering moisture or water of crystallization, the substance should be dried in a desiccator, or by the application of heat, as the case admits, before undertaking the test.

When the substance is of such nature as to readily liquefy and yield a clear solution, no difficulty is likely to be encountered in observing the exact point at which fusion takes place. Some organic substances, however, do not melt without partial alteration, and in these cases the liquefied substance is discolored to a greater or less extent. Other organic substances do not melt except with complete decomposition which is attended by the separation of carbon. Some substances are not affected by heat until it reaches a destructive degree; they may then be converted into fusible products; but the melting points of such substances are not usually regarded as definite. Other substances melt to thick liquids, which upon the application of more heat become perfectly fluid.

The United States Pharmacopœia mentions the melting or liquefying points of some official articles which are ordinarily fluid. The determination of the temperatures at which these substances become liquid may be ascertained as follows. Some of the liquid to be tested is put into a capillary tube, attached to a thermometer in the usual way; the bulb of the latter and the part of the tube containing the material are immersed in a bath of mercury ; the whole is then set in a cooling bath until solidification of the substance being tested takes place, and the thermometer registers a point several degrees below the temperature at which this change occurs. The mercury bath, with the thermometer and capillary tube, is then removed, its temperature allowed to rise, and the point at which liquefaction takes place noted.

DETERMINATION OF CONGEALING POINTS.

Many substances, liquid at ordinary temperatures, may readily be made to solidify or congeal by exposing them to cold. The determination of the point at which this change takes place serves in some instances to identify the substance or indicate its quality.

Some of the most important liquid pharmaceutical substances solidify at temperatures above the freezing point of water, so that immersion in a bath of melting ice will bring about the desired change ; where this bath does not suffice, a mixture of snow, or pounded ice, and salt will be found available for the purpose.

The liquid to be tested is usually put in a narrow test-tube, and the bulb of a thermometer completely submerged in it.

The solidification or congelation is indicated by an opaqueness that makes its appearance in the liquid. The change is sometimes induced by adding to the liquid, which has been cooled to the proper point, a solid particle of some of the same substance which has previously been solidified by cold.

The United States Pharmacopœia sometimes utilizes the application of cold as a test for the presence of water, as illustrated by the following official requirement : "Amyl nitrite should remain transparent, or nearly so, when exposed to the temperature of melting ice (absence of water)."

Exposure to cold is also frequently used as a test for the quality of complex bodies, such as the fixed and volatile oils. Fixed oils are examined by exposure to certain degrees of cold, in order to see whether or not they deposit fats solidifiable at those temperatures. The temperature at which, on inclining the tube, the oil no longer flows, or that at which the separation of solid commences, is called the "cold test." Solid fats are sometimes dissolved in ether, and the solution so obtained examined by subjecting it to cold, in order to distinguish between fats having different solidifying points. Volatile oils are usually tested by cold for the presence of their dissolved solids or stearoptens ; by this means the official oil of peppermint is distinguished from the dementholized oil.

Organic solids are sometimes melted, and the resulting liquid allowed to cool, in order to ascertain the solidifying point. In such cases, a rather large quantity of the substance is cautiously melted in a dish or test-tube, a thermometer inserted, and the heat withdrawn. As the liquid cools the mercury gradually falls in the thermometer, but, when the congealing point is reached, the column remains stationary for a short time, because the crystallization of the material produces enough heat to arrest the cooling. The liquid should be constantly stirred with the thermometer during the cooling.

It is advisable in all cases, as a check on the first result, to carefully remelt the substance and repeat the operation. When this is done the melting point also may be noted; the latter, however, will not always coincide with the solidifying point, nor need it do so in all cases.

DETERMINATION OF BOILING POINTS.

The determination of this constant is a very important matter in the examination of all volatile liquids and of some volatile solids.

The boiling point of a substance is constant for the same atmospheric pressure.

In the case of mixtures of volatile liquids—for example, many of the volatile oils—the boiling point of the whole is not a constant temperature, but, by recourse to the process of fractional distillation, the boiling points of the several constituents may be found.

The best plan of determining the boiling point of a liquid, and one that is adapted to the purpose if fractional distillation needs to be resorted to, is conducted as follows. Some of the liquid is put into a distillation bulb, the delivery tube of which has been attached to a well-cooled condenser. The bulb should not be more than half filled with the liquid. The mouth of the bulb is closed with a cork having a perforation, into which a thermometer has been inserted. The latter must extend so far into the neck that its mercury bulb comes just below the lateral exit for the vapors, but does not dip into the liquid. A receiving vessel is placed at the lower end of the condenser. When these arrangements are completed, heat is applied by suitable means, and gradually increased. The mercury rises in the thermometer, and after a while distillation commences. Constant watch is kept on the mercury column, and the degree of temperature at which it becomes stationary is taken as the boiling point. If the liquid is a single well-defined chemical substance, it will all distil at that temperature. If, however, the temperature rises materially after a portion only of the substance has passed over, the liquid is a mixture, and the process of fractional distillation must be employed to find the boiling points of the several constituents. In this process, portions of the distillate are caught separately at fixed intervals,—say every five or ten degrees; these fractions are then distilled by themselves, and the portions coming over at approximately the same temperatures added together. By repeating the operation several times, the distillates show a tendency to accumulate at a few fixed temperatures corresponding to the boiling points of the components of the original mixture. The process succeeds best, of course, when the boiling points of the individual components are moderately removed from one another.

If the liquid is decomposed by the heat into substances which have lower boiling points than the original material, the mercury column will descend.

The lowest point at which a liquid will boil may readily be found by taking in a test-tube or flask enough of the liquid to cover the bulb of the thermometer, and applying a gradually increased heat, until active ebullition is produced. If the rising mercury column shortly becomes stationary, the height to which it has risen is recorded as the boiling point. This method will usually serve for the determination of the boiling point of most simple, official, volatile liquids.

In some cases the United States Pharmacopœia requires a liquid to boil, when a half test-tubeful of it is heated to a certain point, and a few pieces of broken glass are introduced. Ether is directed to be tested in this manner, the heat being supplied by grasping the tube containing the fluid in the hand. The broken glass is used to induce a regular disengagement of the vapor, and thus prevent the irregular and violent boiling known as bumping.

It is desirable, in the determination of boiling points, to have the stem of the thermometer up to the top of the mercury column immersed in the vapor. Whenever this cannot be done, a correction has to be applied to allow for the part of the column projecting above the vapor. This correction is applied by Kopp in the following manner. The temperature is read off on the thermometer projecting from the apparatus. Another thermometer is clamped in a vertical position, so that its bulb is close to the stem of the first instrument, and the middle of its bulb in proximity to the middle of the projecting part of the mercury column. A horizontal screen is placed around the thermometers to prevent them from being unequally heated by the flame. The corrected temperature is equal to $T + N(T - t) \times 0.000154$, where T is the apparent boiling temperature, t the reading on the second thermometer, and N the length of the projecting mercury column, in degrees of the scale, from the middle of the cork up to T. 0.000154 is the coefficient of expansion for mercury in glass for 1° C.

The boiling point is also dependent upon the atmospheric pressure, as indicated by the barometer (see Volume I. page 40), and, therefore, the pressure must be noted in connection with each boiling-point determination. Landolt states that for pressures not far from the normal (760 mm. at 0° C.) the boiling point is depressed 0.043° C. for each decrease of 1 mm. in the pressure.

DETERMINATION OF THE OPTICAL ROTATION OF ORGANIC SUBSTANCES.

"Many organic substances either liquid by nature or in solution in suitable solvents, when examined in a specially constructed polarizing apparatus or polaristrobometer, exhibit the property of circular polarization, or, in other words, are capable of rotating the plane of polarization of a ray of light either to the right or to the left. Such substances are termed 'optically active,' and when rotating to the right are designated as 'dextrorotatory' or 'dextrogyrate,' and when rotating to the left, as 'lævo-rotatory' or 'lævogyrate.' Substances which do not possess this property of optical rotation are termed 'optically inactive.'

"Among the substances recognized by this Pharmacopœia, there are several, particularly certain essential or volatile oils, and related bodies, for which the determination of the angle of rotation of a ray of polarized light, or, in some cases, the proof of their optical inactivity, affords the most simple and positive evidence of their identity or purity.

"The instruments used for this purpose vary somewhat in their construction. Those which are most suitable for the examination of the substances mentioned above are the polaristrobometer of Wild, in which the optical activity of the substance is manifested by the appearance or disappearance of dark, parallel stripes, and the so-called 'half-shadow' instrument of Laurent, in which the two sides of the field of vision are capable of becoming unequally illuminated. Both of the instruments permit the angle of rotation to be read off in degrees or fractions of a degree of a circle.

"These optical determinations are best made in a dark room, and by means of homogeneous or monochromatic light, the latter being obtained by introducing into a non-luminous flame, on a loop of platinum wire, a small bead of fused sodium chloride. The light thus radiated corresponds with the line *D* of the solar spectrum.

"Since the deviation of the plane of polarization either to the right or to the left of the zero point is directly proportional to the length of the column of liquid, it is important that the observations should be made with tubes of a definite length, such as 100, 50, or 25 millimeters. The selection of the length of the tube to be employed is, however, usually dependent upon the depth of color of the liquid and the extent of its optical rotation.

"The rotatory power of an optically active, liquid substance, observed with sodium light, and referred to the ideal density 1, and in a tube having a length of 1 decimeter (100 mm.), is designated as its specific rotatory power. This is usually expressed by the term $[a]_D$. Since, however, not only the density of an optically active liquid, but also its rotation, is influenced by the temperature, the specific rotation varies with the latter. In stating the specific rotation it is, therefore, necessary to indicate at what temperature the rotation and the density of the liquid have been determined. But for the same temperature the specific rotation of a pure, optically active liquid is always a constant number.

"For calculating the specific rotatory power of an optically active liquid substance, or solution of an optically active solid, the following formulas are of general application:

I. For liquid substances $[a]_D = \frac{100 \times a}{L \times d}$.

II. For solutions of solids

$$[a]_D = \frac{10000 \times a}{L \times P \times d} \quad \text{or} \quad [a]_D = \frac{10000 \times a}{L \times c}.$$

"For calculating these formulas the determination of the following factors is necessary:

a = the angle of rotation of the liquid or solid observed with sodium light.
L = the length of the tube in millimeters.
d = the density or specific gravity of the active liquid.
P = the amount of active substance in 100 parts by weight of the solution.
c = the number of grammes of active substance in 100 cubic centimeters of the solution."—*United States Pharmacopœia.*

The phenomenon of the polarization of light is described in Volume I., where a description of the polariscope also will be found.

Water and alcohol are usually used as solvents for the solid substances.

The temperature directed by the United States Pharmacopœia in the case of volatile oils—the only one in which a certain angle of rotation is required by that authority—is from 15° to 20° C.

In using the polaristrobometer of Wild, the tube, into which the substance is to be put for examination, is filled with distilled water and placed in position between the polarizing and analyzing prisms. The latter is then so adjusted, by turning it with the hand, that the zero mark on the index and that on the scale are seen to exactly coincide, when viewed through the accompanying telescope. When the instrument is in this position, the dark, parallel stripes should not be visible through the eye-piece of the polariscope. The tube is then emptied, thoroughly dried, and completely filled with the liquid to be tested, by carefully pouring the latter down the side so as to avoid the production of air-bubbles; the tube is then securely closed and again placed between the prisms. If the substance is optically active, the dark, parallel stripes will now be visible in the polariscope. To analyze or determine the angle of rotation, the analyzing prism is turned by hand, in the direction opposite to that through which the optically active liquid has turned the light, until the stripes disappear; the rotation required to produce this effect is then read, in degrees or fractions of a degree of a circle on the scale, through the accompanying telescope.

In the case of the Laurent instrument the zero point is reached by turning the analyzing prism until the two sides of the field become equally dark. Upon interposing an optically active liquid, the two halves become unequally illuminated; then by turning the analyzing prism until uniform darkening of the field results, the angle of rotation, in degrees of a circle or fractions thereof, will be indicated upon the scale.

The adjusting screw, which operates the analyzing prism, does so by cogs; hence, when, to find the angle of rotation, the screw is turned in the direction of the course of the hands of a watch, the substance is shown to be dextro-rotatory; and, of course, when turned in the opposite direction, lævo-rotatory.

From the angle of rotation observed, the specific rotatory power (or $[a]_D$) may be calculated by the formulas already given.

CHAPTER IV.

QUANTITATIVE EXAMINATION OF GALENICALS, WINES, SPIRITS, ETC.

DETERMINATION OF THE ALCOHOLIC STRENGTH OF LIQUIDS.

If the liquid be rectified or proof spirit, the percentage strength may be ascertained by taking the specific gravity and referring to the alcoholometrical table on page 315.

The specific gravity may be taken by means of a specific gravity bottle, as described on page 240, or with an accurate hydrometer; if the latter is used, the form prescribed by the United States government for the use of internal revenue and custom-house officers is preferred. In taking the specific gravity of alcohol and alcoholic beverages, the temperature of 60° F. (15.55° C.) is employed, since all the laws and regulations of the United States, referring to alcohol and alcoholic liquids in general, are based on this degree of temperature.

In whiskeys and brandies, in which the amount of extract is trifling, the percentage of alcohol can also be determined with sufficient accuracy by the foregoing method.

The United States Pharmacopœia states that the specific gravity of *whiskey* should not be more than 0.930 nor less than 0.917, corresponding, approximately, to an alcoholic strength of 44 to 55 per cent. by weight, or 50 to 58 per cent. by volume. The specific gravity of *brandy*, according to the same authority, should not be more than 0.941 nor less than 0.925, corresponding, approximately, to an alcoholic strength of 39 to 47 per cent. by weight, or 46 to 55 per cent. by volume.

When, however, the liquids contain an appreciable amount of dissolved solids, the alcoholic strength must be ascertained either according to the method specified by the United States Pharmacopœia for wines, or by distilling off the alcohol, then making the distillate up to the original volume with water, taking the specific gravity of this mixture in the usual way, referring to the table, and calculating the alcoholic strength of the original sample, as shown on page 254.

To conduct the former of these methods proceed as follows: "Take the specific gravity (to four decimals) of a sufficient portion of the wine carefully measured at the temperature of 15.5°, evaporate the wine in a tared capsule to one-third of its original weight, cool, and add water until the liquid measures its original volume at 15.5°; then take the specific gravity (to four decimals) again. The difference between the two specific gravities deducted from 1.0000 corresponds to the specific gravity of an alcohol containing the same percentage of absolute alcohol, by weight or volume, as the wine under examination, the corresponding percentage being ascertained by referring to the alcoholometrical table [given on page 315]."

Before taking the specific gravity of beer and effervescing wines, the carbon dioxide must be got rid of as far as possible by shaking the sample in an open vessel.

The United States Pharmacopœia specifies that the specific gravity of *white wine* should not be less than 0.990 nor more than 1.010; and when tested by the foregoing method, it should be found to contain not less than 10 nor more than 14 per cent., by weight (equivalent to 12.4 to 17.3 per cent. by volume), of absolute alcohol. The same authority requires that the specific gravity of *red wine* should not be less than 0.989 nor more than 1.010; and when tested by the official method, it should be found to contain not less than 10 nor more than 14 per cent., by weight (equivalent to 12.4 to 17.3 per cent. by volume), of absolute alcohol.

To determine the percentage of alcohol by the distillation method, 100 cubic centimeters of the sample are diluted to about 150 cubic centimeters with water. When free acids are present, especially volatile ones, it is customary to neutralize them in the portion taken for distillation by the addition of sodium hydrate solution. The mixture is then placed in a flask supported on a wire gauze, and distilled, with the aid of a condenser, into a graduated vessel, until 100 cubic centimeters have passed over. The tendency of some wines to foam during the distillation may be overcome by the addition of 0.1 gm. of tannin to each 100 c.c. The distillate is then thoroughly mixed, cooled to 15.5°, brought exactly to the 100 cubic centimeter mark by the addition of water, and again mixed. Its specific gravity is now taken, and, from the alcoholometrical table on page 315, the percentage of alcohol by weight of the distillate found. The percentage by weight in the original sample is then found by the following proportion: as the specific gravity of the original sample is to the specific gravity of the distillate so is the weight per cent. in the distillate to the weight per cent. in the original sample.

The foregoing methods are, of course, applicable to the determination of alcohol in fluid extracts, tinctures, and similar pharmaceutical products, due regard being had for the presence of interfering substances.

DETERMINATION OF THE ACIDITY OF AQUEOUS AND ALCOHOLIC LIQUIDS.

The simple determination of the most important acids in aqueous solutions is described under volumetric processes. The estimation of the acidity of aqueous and alcoholic solutions in general may be conducted in a manner similar to the one described in that place. The outline of this method is that a measured or weighed portion of the solution to be tested is taken, a few drops of an appropriate indicator added, and the solution titrated with volumetric alkali solution until neutralization is indicated. The foregoing process by itself is not sufficient, of course, if more than one acid-reacting substance is present. The preliminary qualitative analysis will decide this matter; and if more than one such substance is present, means must be devised to effect their individual estimation, or the total acidity calculated into terms of the most important acid present, or the acidity is expressed by stating the number of cubic centimeters of the standard alkali required for a given volume of the liquid. While the several acids may usually be separated and estimated by some means or other, for many purposes, it is not necessary to undertake this. Where part of the substances causing the acidity are volatile with water vapor, and part non-volatile, the amount of each form may easily be estimated. This is done by first titrating a portion of the original solution, then evaporating an equal portion of the same to dryness in order to expel the volatile acid, dissolving the residue in water, and titrating the non-volatile acid-reacting substance. By deducting the volume of alkali solution required for the latter from that required for the total acidity, the volume of alkali solution neutralized by the volatile acids is found. Such a course is pursued in the examination of beer and wine. In these cases any considerable quantity of carbon dioxide is to be first removed by agitating the sample in an open vessel.

The United States Pharmacopœia places the following limits of free acid on the official wines and spirits:

"To neutralize 50 c.c. of *white wine* should require not less than 3 nor more than 5.2 c.c. of normal potassium hydrate V. S., phenolphtalein being used as indicator."

"To neutralize 50 c.c. of *red wine* should require not less than 3 nor more than 5.2 c.c. of normal potassium hydrate V. S., eosin or fluorescein being used as indicator."

"To render 100 c.c. of *brandy* distinctly alkaline to litmus should require not more than 1 c.c. of normal potassium hydrate V. S."

"To render 100 c.c. of *whiskey* distinctly alkaline to litmus should not require more than 1.2 c.c. of normal potassium hydrate V. S."

The total acidity of wine is calculated into tartaric acid, as are also the non-volatile acid-reacting substances; the volatile acids are calculated as acetic acid.

The acidity of whiskey and brandy is stated in acetic acid.

The volatile acidity of beer is also calculated into acetic acid, while the non-volatile acid-reacting substances are given in terms of lactic acid.

In some cases the acidity allowable in a liquid is tested by adding a specified quantity of the liquid to a specified volume of a volumetric alkali solution which has been previously tinted with an indicator; if the color persists, the acidity is within the limit.

Of course, some solids which are liable to contain free acids may be dissolved and tested by the foregoing methods; water and alcohol are preferred as solvents in such cases. But in the event of the substance being insoluble in either of these liquids, chloroform or ether may be tried, and in some instances the solution prepared with these liquids will admit of dilution with alcohol. Where the solvent is immiscible with the alkali solution, it is obviously necessary to thoroughly shake the liquids together.

The acidity of liquids is sometimes estimated by neutralization with potassium bicarbonate. For this purpose, a weighed portion of that salt in fine powder is taken, and, little by little, added to a measured volume (usually one fluidounce) of the liquid, while effervescence is caused by more of it. The unused salt is then weighed, and, by subtracting its weight from that of the original portion, the amount required to neutralize the liquid is found. This plan is still used occasionally to test vinegar; and the quantity of potassium bicarbonate needed to neutralize a fluidounce of vinegar is referred toin the trade as *grains per ounce.*

DETERMINATION OF EXTRACTIVE AND ASH IN LIQUIDS.

The estimation of dissolved non-volatile matter is often required in the examination of fluid preparations like the galenicals, and is especially observed in the analysis of wines, spirits, and other alcoholic beverages. The usual process is to evaporate a known weight of the liquid, in a tared dish, at a suitable temperature, on a water-bath. The evaporation should be performed below the boiling point of the liquid. After dryness is reached, the bath is brought to boiling and the heating prolonged until the weight of the dish and residue is constant; in some cases it is necessary to transfer the dish and residue to an air-bath and complete the drying at 110°. The increase in weight over that of the dish gives the amount of total solids or extractive in the quantity of original liquid taken. The result is calculated into percentage by weight. If it is desired to find the solids in a given measure of a liquid, a definite volume of the original material is evaporated in the manner described. This plan is adopted in the examination of beer, spirits, and wines; in these cases the solids are calculated into percentage on the volume, the latter in cubic centimeters being assumed as grammes. The foregoing process is, of course, applicable in all cases where the solvent is volatile under the conditions given. If glycerin is present in the liquid, there will be a trifling loss of it during the process through its volatilization by the steam. After determining the weight of the residue, obtained by evaporation, it may be analyzed qualitatively and quantitatively. The United States Pharmacopœia prescribes limits to the amount of non-volatile solids or extractive in the official spirits and wines, as follows:

"If 100 c.c. of *brandy* be very slowly evaporated in a tared capsule on a water-bath, the residue, when dried at 100°, should not weigh more than 1.5 gm."

"If 100 c.c. of *whiskey* be very slowly evaporated in a tared capsule on a water-bath, the residue, when dried at 100°, should not weigh more than 0.25 gm."

"If a portion of *white wine* be evaporated, the residue, when dried during twelve hours on a water-bath, should not amount to less than 1.5 nor more than 3 per cent."

"If a portion of *red wine* be evaporated, the residue, when dried during twelve hours on a water-bath, should not amount to less than 1.6 per cent. nor more than 3.5 per cent."

50 c.c. of a sample of wine, measured at 15.5°, are usually taken for the evaporation.

After determining the total solids, it is frequently advisable to estimate the organic solids and the ash. The estimation of these is accomplished by carefully igniting the residue of total solids according to the directions given on page 206. The loss on ignition, in the absence of interfering substances, as stated in the place cited, is taken as organic solids; the residue in the dish or crucible represents the fixed inorganic matter or ash of the liquid.

DETERMINATION OF GLYCERIN IN AQUEOUS AND ALCOHOLIC LIQUIDS.

It is frequently desirable to know the amount of glycerin which is present in a pharmaceutical preparation or in an alcoholic beverage.

The exact determination of glycerin in such liquids is beset with many difficulties. An approximate estimation will answer the purpose in most cases, and may usually be effected as follows. Slaked lime, in slight excess, is added in a porcelain dish to a definite quantity (volume or weight, as required) of the liquid to be tested, and the mixture evaporated to dryness by a gentle heat. The residue is treated with successive, small portions of alcohol, which are boiled by the heat of the water-bath, and thoroughly mixed with the residue; after each treatment, the insoluble matter is allowed to subside, and the alcoholic solution decanted upon a filter. Four or five such applications are made. The filtered, alcoholic solutions are mixed, the solvent evaporated by heating on a water-bath, and the residue of glycerin dried for about an hour. It is then weighed or measured. The lime forms, with carbohydrates, many organic acids and various extractive matters, combinations which are insoluble in alcohol, and thus prevents the removal of these substances by that solvent. Lead oxide and zinc carbonate are sometimes used for similar purposes, and occasionally may prove useful if used in connection with the slaked lime.

Usually the glycerin obtained in this manner is moderately pure; it is not absolute glycerin, however, but, in strength, more nearly approaches the commercial article. Frequently it can be purified by dissolving it in a measured volume of absolute alcohol, and mixing the solution, so obtained, with one and a half times as much ether, by volume, as of alcohol used; any insoluble matter that separates is removed by filtration, the filter washed (with a mixture of absolute alcohol two volumes and ether one volume), and the filtrate and washings evaporated, as before, to obtain the purified glycerin for measuring or weighing. Finally, the glycerin should always be tested for such impurities as may be suggested by the nature of the substances with which the glycerin was originally mixed, and, if such be found present, an allowance made for them.

Glycerin may be also estimated by the method of Benedikt and Zsigmondy, which depends upon the fact that, in alkaline solution, glycerin is oxidized to oxalic acid by potassium permanganate. This method, however, cannot be directly applied in the examination of fluids containing other organic matters which are oxidizable to oxalic acid; in fact, it is almost limited in applicability to plain aqueous solutions of glycerin. Alcohol and extractive matters are examples of substances which interfere with the general applicability of the method; hence the process cannot be employed for the estimation of glycerin in such liquids as fluid extracts and wines without first removing the alcohol by evaporation, and subsequently separating the glycerin from the extractive matters, as in the method already given. If now the residue of glycerin is free from other substances capable of yielding oxalic acid under the conditions of the test, the actual glycerin in it may be estimated as follows. A weighed quantity (from 0.2 to 0.3 gm.) of the residue is dissolved in about 250 c.c. of water. The resulting solution is made strongly alkaline with potassium or sodium hydrate, and then treated with enough powdered potassium permanganate to cause it to assume a blue or blackish appearance. The solution so colored is boiled for an hour, water being occasionally added to it to prevent concentration. At the end of that time, sufficient of a strong solution of sodium sulphite to decolorize the liquid is added. The liquid, while yet hot, is filtered to remove the precipitated manganese dioxide, and the latter is well washed with boiling water. The filtrate and washings are collected together, allowed to cool, then acidified with acetic acid, and afterwards precipitated with calcium chloride. After the calcium oxalate has completely settled, it is collected in a funnel closed by a small plug of asbestos, and there washed with water. Then it is rinsed, by means of a jet of water, along with the asbestos, into a beaker or dish. Enough concentrated sulphuric acid to impart a decided warmth to the liquid is now added to the contents of the vessel; and, after this addition, sufficient decinormal potassium permanganate volumetric solution to establish a permanent pink tint is run in from a burette. Each cubic centimeter of the decinormal volumetric solution required for this purpose represents 0.0045895 gm. of glycerin.

The oxidation of the glycerin by the potassium permanganate may be most conveniently explained by assuming the latter to be composed of equal molecules of potassium oxide and permanganic oxide; the last of these compounds supplies the oxygen required, each molecule of it, in alkaline solution, giving off three atoms of this agent, at the same time being reduced to two molecules of manganese dioxide. The oxygen acts upon the glycerin according to the following equation, converting it into oxalic acid, carbon dioxide, and water:

$$C_3H_5(OH)_3 + O_6 = H_2C_2O_4 + CO_2 + 3H_2O.$$

The free alkali present at once reacts with the oxalic acid and carbon dioxide, forming the corresponding potassium salts.

All the other reactions of the process are either written or illustrated by similar ones, under appropriate headings, elsewhere in this volume.

In order to sum up the quantities of glycerin and potassium permanganate involved, the changes which take place during the oxidation of the former in alkaline solution may be expressed by the single equation:

$$C_3H_5(OH)_3 + 2K_2Mn_2O_8 = K_2C_2O_4 + K_2CO_3 + 4MnO_2 + 4H_2O.$$

PART IV.

URINE ANALYSIS.

CHAPTER I.

THE PHYSICAL CHARACTERS OF URINE.

General.—Urine is an animal fluid separated from the blood by the kidneys. When recently voided it is transparent and of a straw-yellow color. Its odor is very properly described as urinous, and is modified by certain articles of diet, as asparagus, and by some medicinal substances, notably turpentine. The reaction of urine is usually distinctly acid to litmus, although it may be neutral or alkaline, according to the diet or to the time which has elapsed after partaking of food. After standing a few hours it becomes cloudy, owing to separation of phosphates, the amount of precipitate being increased as the urine becomes alkaline from decomposition with formation of ammonia. The time for collecting the sample for analysis is left to the judgment of the physician in charge of the patient. Unless for special reasons, the urine should be examined as soon after being voided as possible.

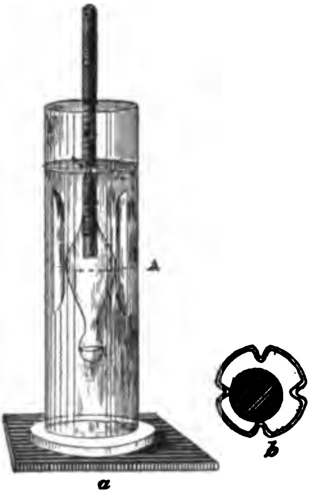
Quantity.—The amount of urine passed in twenty-four hours is variously stated to be from 1200 to 1500 c.c. The quantity is modified by a variety of conditions and circumstances ; much depends on the temperature of the atmosphere, whereby the secretion of liquid by the skin is increased or decreased ; similarly, the amount of exercise indulged in by the individual will cause a variation, for the same reason ; the amount of liquid taken also has a direct effect on the quantity of urine secreted.

Color.—The color is very much influenced by the amount passed. An abundant urine is usually light in color, the substances which impart color being diluted; and a scant urine, being concentrated, is dark in color. The shade varies from a dark yellowish brown to a very light straw-yellow. Certain organic substances when taken internally affect the color, notably santonin, which imparts a yellowish shade.

Specific Gravity.—Normal urine may vary in specific gravity from a number of causes similar to those which affect the quantity in twenty-four hours; it may vary from 1.010 to 1.030, the average being 1.020 at 15° C., compared with water at the same temperature.

The specific gravity of urine is most easily determined by the *urinometer*. This instrument is similar in construction to the ordinary hydrometer; the stem is graduated from 1.000 to 1.050. The apparatus devised by Dr. Squibb for this purpose has many improvements which make it the most desirable. (See Fig. 14.) *a* represents the urinometer floating in the urine. *b* is a cross-section of *a* in the plane of the dotted line *A;* it shows the usefulness of the indentations, on the sides of the cylinder, in preventing incorrect readings through the urinometer clinging to the sides of the vessel. The urinometer is used by placing in the cylinder enough urine to float the instrument, which is then carefully introduced. When the urinometer has come to rest, the eye is brought on a level with the surface of the urine in the vessel, and the specific gravity read at the point on the graduated scale of the instrument where a horizontal line drawn from the general level of the surface at the bottom of the curve intersects the stem.

FIG. 14.



Since the specific gravity of liquids is influenced by heat, through the expansion and contraction of their volumes, the temperature of the urine must be taken immediately after the reading of the specific gravity, and, if the sample has not the standard temperature of 15° C., the specific gravity must be corrected for that temperature, in order that results may be compared. The temperature is found by removing the urinometer from the cylinder and introducing a thermometer into the urine; when the height of the mercury column becomes constant, the degree of temperature is read off. For every 3° C. above 15°, add .001 to the reading, and for every 3° below 15°, subtract .001 from the reading. On the Fahrenheit scale 60° is the normal temperature, and for every 5.4° F., .001 must be added to or subtracted from the reading.

Total Solids in Urine.—The amount of solid matter in urine bears a close relation to the specific gravity. It has been found that in a large majority of samples the last two figures of the specific gravity multiplied by 2.33 (Hæser's coefficient) will give the number of grammes of solid matter in a liter of the urine, measured at the temperature at which the specific gravity was taken. For example, a sample having the gravity 1.021 would contain in each liter $21 \times 2.33 = 48.93$ grammes ; supposing the patient to have passed 1425 c.c. during twenty-four hours, the amount of solids excreted during that time would be :

$$1000 : 1425 :: 48.93 : x = 69.72 \text{ grammes.}$$

To obtain the data for the last of these calculations, the urine is measured at the ordinary temperature, the exact temperature of the urine taken, and the specific gravity calculated for the latter temperature.

The coefficients 2 and 2.2 have been given, but 2.33 appears to have the weight of authority in its favor.

The practical method of determining the solids in urine is by evaporating, under reduced pressure, a weighed portion (about 5 grammes) in a platinum dish over sulphuric acid, or other dehydrating agent, in a desiccator, and finally removing to an air-bath and drying at 100° to constant weight. The object in first drying at ordinary temperature is to reduce as much as possible the chances for decomposition of the urea, and consequent loss on that account.

The average total amount of solids in the urine of an adult during twenty-four hours is about 60 grammes, or from 4 to 5 per cent.

CHAPTER II.

THE COMPOSITION OF URINE.

I. NORMAL CONSTITUENTS.

THE following percentage amounts of the normal solid constituents of human urine have been given by Parkes:

	Per Cent.
Urea, CH_4N_2O	45.75
Creatinine, $C_4H_7N_3O$	1.25
Uric Acid, $C_5H_4N_4O_3$	0.75
Hippuric Acid, $C_9H_9NO_3$	0.55
Pigment and other organic substances	13.79
Sulphur Trioxide, SO_3	2.77
Phosphorus Pentoxide, P_2O_5	4.36
Calcium	0.35
Magnesium	0.28
Potassium	3.45
Sodium	15.29
Chlorine	10.35
Ammonia	1.06
	100.00

The foregoing analysis probably fairly represents the average composition of urine, but it takes no account of the variations in composition resulting from change of food or from other causes.

The physical and chemical properties of the substances enumerated in the table will be found in Volume I.

ORGANIC NORMAL CONSTITUENTS.

The best known and most definite of the coloring matters of normal urine is urobilin $(C_{16}H_{18}N_2O_3)_2H_2O$; urine-indican, another pigment, is not well understood. Xanthine, $C_5H_4N_4O_2$, and allantoin, $C_4H_6N_4O_3$, are also constituents of normal urine, and, together with urea, creatinine, and uric acid, constitute its five chief constituents of the nitrogenous type. The other organic substances are mainly simple and complex acids and nitrogen derivatives of them.

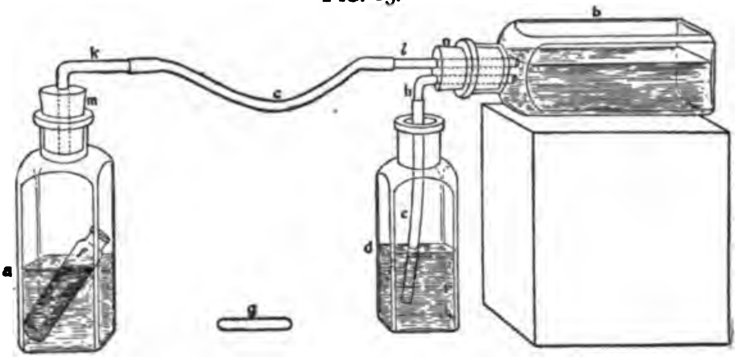
Urea.—Urea, or carbamide, $CO(NH_2)_2$, is the most important of the solid constituents of urine. It constitutes from 2 to 2.5

per cent. of normal urine. The average quantity excreted by an adult in twenty-four hours is 30 grammes. The amount ranges between 20 and 40 grammes, depending on the quantity of nitrogenous food taken, as well as the destruction of tissue, as, for instance, in fever; when the amount of urea is increased.

Urea forms, almost always, about 90 per cent. of the nitrogen contained in the normal urine.

Sodium hypobromite and hypochlorite decompose urea into carbon dioxide, nitrogen, and water, and advantage is taken of this reaction for the estimation of urea. For this purpose, the convenient method and simple apparatus proposed by Squibb will be found sufficiently accurate for the needs of every-day practice. Fig. 15 represents the apparatus at the end of a determination, while standing to allow of adjustment of temperatures before measuring the result. *a* and *b* are square, wide-mouthed vials, of about 120 cubic centimeters' capacity. They are fitted with stoppers, *m* and *n*, provided with the glass tubes, *h*, *k*, and *l*, as shown in the illustration. Although ordinary corks are suitable, rubber stoppers are better and more durable. If ordinary corks be used, they should previously be thoroughly soaked in water in order to make the apparatus air-tight. If rubber stoppers be used, they should be put in dry, the mouth of the vial being also dry; otherwise they are difficult to keep in place. *c* is a piece of rubber tubing of about 3 millimeters' bore and about 20 centimeters long. *d* is a vial capable of holding 60 cubic centimeters. *e* is a rubber tube, similar to *c*, slipped onto the bent glass tube, *h*, and long enough to reach to the bottom of *d*. *f* is a homœopathic vial of about 5 cubic centimeters' capacity.

FIG. 15.



The estimation is conducted as follows, beginning with the apparatus disconnected and empty. Put into vial *a* 40 cubic centimeters of official solution of chlorinated soda. Measure accurately into the homœopathic vial, *f*, 4 cubic centimeters of the urine to be tested, and by means of forceps place the charged vial in the solution contained in vial *a*, in the position shown in the cut, and put the stopper, *m*, securely in place, having the rubber tube, *c*, slipped onto the bent glass tube, *k*. Fill vial *b* nearly full of water having the temperature of the room. Put the rubber tube, *e*, on the bent glass tube, *h*, and then put the stopper, *n*, firmly in place. Then, holding vial *b*, thus stoppered, in the right hand, with the forefinger over the end of the straight glass tube, *l*, incline the vial towards the bent glass tube, *h*, until that and the attached rubber tube, *e*, fill with water. When these are filled, stop the flow by closing the end of the straight tube, *l*, with the forefinger, and with the left hand put the plug of glass, *g*, into the end of the rubber tube, *e*, while this tube is full of water. Then lay the vial, *b*, on its support, as shown, and slip the free end of the rubber tube, *c*, onto the straight glass tube, *l*, thus connecting the vials *a* and *b*. Put a dish under the end of the rubber tube, *e*, and then take out the plug, *g*. A few drops of water will usually escape, but if the apparatus be tight, and if the temperature of the apparatus and the room be the same, no more water will run out, nor will any air enter. Throw away the water that collected in the dish. Now rinse out the vial, *d*, and drain it for a minute, so as to leave the inner surfaces as wet as they will be left when the vial is emptied for measurement of the water which it is intended to receive. Then put the vial in its place under the rubber tube, *e*, as shown, letting the rubber tube extend to the bottom of the vial. The apparatus is then ready for the process.

Incline the vial, *a*, until the urine and the solution of chlorinated soda mix, and agitate the mixture gently sidewise until the effervescence ceases, being sure that a full interchange of liquids between the homœopathic vial and vial *a*, containing it, is effected.

The decomposition of the urea takes place according to the following equation:

$$CO(NH_2)_2 + 3NaClO = CO_2 + 3NaCl + 2H_2O + N_2.$$

The carbon dioxide is at once absorbed by the excess of sodium carbonate in the solution of chlorinated soda. The sodium chloride and water also remain in the solution in vial *a*. The nitrogen which is liberated, however, either passes over into vial *b* or forces an equal volume of air from *a* to *b*, in either case displacing its own volume of water, which passes out into *d*. It is hardly necessary to say that, if the water in *b* falls below the upper level of the bent tube, *h*, the operation must be repeated with a smaller volume of urine. When the effervescence is at an end, and no further movement of gas into *b* occurs upon vigorous agitation of *a*, let the apparatus stand from a quarter to half an hour, in order that it may regain the room temperature, and the expansion of the nitrogen by the heat of the reaction be corrected. During this cooling, a little water, whose bulk equals the increase in volume of the nitrogen through the effect of the heat referred to, will pass back from *d* into *b*, and in some cases from *b* into *a*. When this movement ceases, the water in *d* is to be carefully measured, for which purpose it is poured into a dry, graduated cylinder. If a cylinder of suitable dimensions is at hand, the water may be collected in it instead of in the vial; the cylinder should be employed dry. Each cubic centimeter of water displaced by the nitrogen is practically equal to one cubic centimeter of nitrogen, and one cubic centimeter of nitrogen represents 0.00267 gramme of urea. From the quantity of urea represented by the water displaced and the weight of the 4 cubic centimeters of urine, the percentage of urea is then calculated. For example, suppose the displaced water from 4 cubic centimeters of urine be 30 cubic centimeters. Then 30 times 0.00267 gramme is 0.0801 gramme, or the amount of urea indicated. Supposing that the specific gravity of the urine at the temperature at which the 4 cubic centimeters were measured is 1.020, then, since the weight of a liquid in grammes can be found by multiplying its volume in cubic centimeters, measured at a given temperature, by its specific gravity at the same temperature, the 4 cubic centimeters will weigh 4.080 grammes. The percentage of urea is then found by proportion as follows:

$$4.080 : 0.0801 :: 100 : 1.96 \text{ per cent.}$$

It is not pretended that any very great degree of accuracy is attained by means of the foregoing process; but, with moderate care, the readings will generally be within 1 c.c. of the true quantity, and this is within 0.07 per cent. in the proportion of urea found.

Creatinine.—Creatinine, $C_4H_7N_3O$, and creatine, $C_4H_9N_3O_2$, are both constituents of normal urine, and are subject to interchange into each other according to certain conditions. In alkaline urine creatine appears in greater quantity, while the reverse is the case with strongly acid urine. Physiologically, the two substances may be considered as one body, although chemically they differ, creatine containing one molecule of water more than creatinine. Since urine is generally acid, creatinine is usually considered the normal constituent.

Creatinine is a strong base, showing a distinctly alkaline reaction to litmus paper. It crystallizes in large, colorless prisms, is soluble in alcohol and in water, but almost insoluble in ether. It is excreted to about the same amount as uric acid, 0.05 to 0.09 gramme being voided in twenty-four hours. It is excreted in increased amount on a meat diet.

With zinc chloride, creatinine gives characteristic groups of fine needles consisting of a combination of the two substances. The production of this combination is used for the detection and determination of creatinine. Creatinine-zinc chloride, $ZnCl_2 . 2C_4H_7N_3O$, is obtained as a precipitate by adding a concentrated aqueous or alcoholic solution of zinc chloride to urine. The crystals are sparingly soluble in water, but practically insoluble in alcohol. To estimate creatinine, a definite volume (say 500 cubic centimeters) of the urine is nearly neutralized with milk of lime, then mixed with calcium chloride, and the mixture evaporated to dryness on a water-bath, the reaction being maintained neutral or faintly acid by cautious addition of acetic acid. The residue is extracted with alcohol saturated with sodium acetate. The solution of creatinine so obtained is cooled and filtered; it is then precipitated with an alcoholic solution of zinc chloride. After twenty-four hours, the precipitate is collected on a filter, washed with alcohol, and drained. The contained creatinine is then deduced from the amount of ammonia obtained by subjecting the precipitate to Gunning's modification of Kjeldahl's method of estimating nitrogen. For this purpose, the precipitate and filter are put into a flask and treated with sulphuric acid, as described on page 312.

As one molecule, or 112.87 grammes, of creatinine, $C_4H_7N_3O$, yields three molecules, or 51.03 grammes, of ammonia, NH_3, each cubic centimeter of normal volumetric acid neutralized by 0.01701 gramme of ammonia, from the precipitate, must represent 0.03762 gramme of creatinine. The total quantity of the substance and its percentage amount are then calculated in the regular way.

Uric Acid.—In normal urine uric acid, $C_5H_4N_4O_3$, is always in combination with potassium, sodium, and ammonium, and sometimes with calcium and magnesium.

In twenty-four hours from 0.2 to 1 gramme of uric acid is excreted, the average quantity being 0.6 gramme. In health the proportion of uric acid to urea is about one to fifty.

Uric acid and acid urates are detected in the sediment of the urine by means of the microscope.* Normal urine rarely shows them until after standing for some time, but in certain abnormal urines they are distinctly visible in the freshly voided specimen. The crystals of uric acid are almost invariably highly colored when deposited from urine. They assume various shapes, the sheaf, whetstone, and lozenge-like forms being among the most common and characteristic; the dark color distinguishes them from other crystals. On account of the color of the sediment it is often called "brick-dust," "red pepper grains," etc. To detect uric acid, the so-called ***murexide test*** is applied. For this purpose, some of the sediment is evaporated to dryness in a porcelain dish on a water-bath, with a few drops of nitric acid, and the cool residue treated with a drop or two of ammonia water. The formation of a beautiful purple color upon the addition of the ammonia indicates uric acid. Urine may be tested by first evaporating a small quantity to dryness in a porcelain dish on a water-bath, and then treating the residue in the manner described for the sediment. The explanation of the test is that the uric acid is oxidized by the nitric acid to alloxan and alloxantin, which in turn are converted into purpuric acid by the first action of the ammonia, while by the further action of ammonia an ammonium salt of purpuric acid is formed. This is the colored substance known as murexide. When much uric acid is present, a yellowish or reddish residue is obtained by simple evaporation with nitric acid; this color is ascribed to alloxantin, but must not be regarded as the evidence sought.

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* To obtain the sediment, the urine is allowed to stand in a clean, conical glass vessel for the undissolved substances to settle, and the supernatant liquid afterwards carefully decanted from the deposit in such a way as not to disturb the latter. A small portion of the sediment is then transferred to a clean glass slide by means of a clean pipette or glass tube, and examined by means of a half- or quarter-inch objective. A cover glass is unnecessary. In a complete examination of urine, the sediment is always examined microscopically and microchemically. The list of substances which can be readily detected by such means includes uric acid, urates, calcium carbonate, oxalate, oxalurate, phosphate, magnesium ammonium phosphate, cystine, leucine, tyrosine, fat, mucus, pus, blood, and various other cellular and extraneous matters. For the identification of urinary deposits see Tyson's "Practical Examination of Urine."

The nitric acid prescribed in the foregoing test may be replaced by bromine water, or the material to be tested may be evaporated with a few drops of hydrochloric acid and a small crystal of potassium chlorate, with the same result.

These tests do not distinguish between uric acid and urates.

Some other substances, notably caffeine and theobromine, give reactions analogous to that of uric acid. They may be distinguished by the fact that the color of the murexide is changed to blue by the addition of potassium hydrate, while the color of the murexoin given by the other substances is destroyed by the same treatment.

The estimation of uric acid in urine is effected by adding to a measured quantity of urine (usually from 200 to 250 c.c.) one-tenth its volume of official hydrochloric or nitric acid, and setting the mixture in a cool place for twenty-four hours. The uric acid separates in highly colored crystals upon the sides and bottom of the beaker. It is collected on a balanced filter and washed with cold distilled water. The filter and uric acid are then dried to a constant weight at 100° C. Since uric acid is very slightly soluble in aqueous liquids, the result is only approximate; it is, however, sufficiently close for practical purposes.

INORGANIC NORMAL CONSTITUENTS.

The inorganic constituents of urine consist chiefly of the chlorides, phosphates, and sulphates of sodium, ammonium, potassium, magnesium, and calcium. Small quantities of iron, silica, and fluorine are also present, and occasionally carbonates are found; the last, of course, impart alkaline reaction. (See pages 261 and 285.) The total amount of these salts varies from 9 to 25 grammes per day.

Chlorine.—The chlorine exists chiefly as sodium chloride, together with some potassium and ammonium chlorides. The amount of chlorides excreted by a healthy adult in twenty-four hours is from 10 to 16 grammes, representing from one-half to one per cent. of the urine. These substances, therefore, next to urea constitute the principal solid constituents of the urine. The usual methods of detecting and estimating chlorine by means of silver nitrate are applicable to urine, although in the quantitative process it is necessary to first remove the albumin by boiling and filtering, as described on page 279. The addition of silver nitrate solution in excess and its residual titration with potassium sulphocyanate solution, as described on page 187, is the plan favored for volumetric estimation. The result is calculated from the weight of silver chloride in the gravimetric method, or the volume of silver nitrate volumetric solution required for complete precipitation when titration is employed. The result is usually expressed in terms of sodium chloride.

Sulphur Trioxide.—The average amount of sulphates passed in twenty-four hours is from 1.5 to 3 grammes. The sulphuric acid radical is detected by the usual test with a soluble barium salt in the presence of hydrochloric acid. (See page 58.) The sulphur trioxide is estimated according to the directions given on page 118.

Phosphorus Pentoxide.—The phosphates present in urine are divided into two classes,—to wit, alkaline and earthy; the former of these are the phosphates of sodium, ammonium, and potassium; the latter, the phosphates of magnesium and calcium. The average quantity of total phosphates voided in one day by an adult is 2.8 grammes. The phosphorus pentoxide may be detected by the usual test with ammonium molybdate. (See page 58.) The phosphorus pentoxide of the earthy phosphates may be separated and estimated by making a definite volume of the urine distinctly alkaline with ammonium hydrate, warming gently, filtering off the precipitate, and washing it with warm water; the washed precipitate is then treated either by the ammonium molybdate or the alkaline magnesium citrate method, as described on pages 122 and 123, for the estimation of the phosphorus pentoxide. The filtrate and washings from the precipitate of earthy phosphates are mixed and precipitated with magnesia mixture, by the directions given on page 121, for the estimation of the phosphorus pentoxide existing in combination with sodium, potassium, and ammonium.

Total Acidity.—The acid reaction of urine is said to be due mainly to monosodium orthophosphate, but it is also contributed by the acid salts of uric and oxalic acids, and, under certain conditions, by free uric, hippuric, lactic, and acetic acids. The total acidity of urine may be determined by placing 50 cubic centimeters of the specimen in a beaker, adding a few drops of phenol-phtaleïn test-solution, as indicator, and titrating with decinormal potassium hydrate volumetric solution until a permanent pink tint is just perceptible. Some analysts state the result in terms of oxalic acid; others calculate it into uric acid; but, on account of the uncertain character of the mixed acid constituents, it is best to say that some definite volume (usually 100 cubic centimeters) of the urine requires such a number of cubic centimeters of decinormal potassium hydrate volumetric solution. In case the urine is so highly colored as to make the end reaction difficult to see, a portion of it should be decolorized by shaking with some animal charcoal. A definite volume may then be filtered for the titration, which usually now succeeds without further trouble.

II. ABNORMAL CONSTITUENTS.

The chief abnormal constituents of urine upon which diagnostic significance is put are albumin, peptone, bile, blood, and glucose. Occasionally the alkaline reaction of freshly voided urine is investigated.

Albumin.—The occurrence of albuminoid matter in urine is known as albuminuria, and is a symptom of Bright's disease.

Serum-albumin, serum-globulin, hemialbumose, and peptone are the albuminoids which occur as abnormal constituents of urine. Of these, serum-albumin is the one most frequently found. Albumin may be detected by a variety of means, the most practical and accurate of which are its coagulation by heat, by nitric acid, by picric acid, by mercuric potassium iodide, and by acidulated brine.

The first two tests will usually prove sufficient to establish the presence or absence of albumin; and yet, while this is true, it is safer to supplement them with the other tests, with a view to confirming the results, and thereby securing additional evidence. In all instances, where the urine to be tested is not perfectly clear, it should be filtered before applying the tests.

The test of coagulation by heat is conducted by pouring about 10 cubic centimeters of the filtered urine into a test-tube, adding two or three drops of official acetic or nitric acid, and warming the tube over a small flame in such a way that only the upper portion of the fluid will be heated; this portion is eventually brought to boiling. In the presence of albumin the urine will become turbid; the turbidity, which can be easily recognized by comparing the two portions of the urine, being in direct proportion to the amount of albumin present. If a large quantity of albumin is present, a flocculent precipitate will be obtained. The small quantity of acetic or nitric acid is intended to prevent the precipitation of the earthy phosphates. If a precipitate is caused in the cold urine by the acid added for the said purpose, it is due to mucin, which is frequently, if not always, present to a greater or less extent in the urine of apparently healthy persons ; in such cases the urine must be filtered before applying heat for the coagulation of the albumin. Whether a turbidity is produced in the foregoing test or not, it is advisable, as a confirmation of the test, to continue the boiling and to add more nitric acid, a few drops at a time, until 15 or 20 drops have been used. This course is rendered necessary by the fact that if a drop or two of acetic or nitric acid be added to a specimen of albuminous urine so as to render it distinctly acid, it may happen, on boiling the urine so treated, that no turbidity or precipitate whatever will appear, although much albumin is present. This is because the serum-albumin has been converted into acid albumin, which is not coagulated by heat, but which is thrown out of solution by a larger quantity of acid. On the other hand, should the quantity of albumin be very small, too much acid will dissolve it permanently. If no turbidity, or only an indistinct one, is obtained upon applying the test, the tube should be set aside for a few hours in order that any minute quantity of albumin may subside and become distinctly visible.

The coagulation of albumin by nitric acid is brought about by the so-called *contact method*. For this purpose, about 2 cubic centimeters of official nitric acid are put into a test-tube, and, the latter being held in a nearly horizontal position, a few cubic centimeters of the urine are slowly poured down the side of the tube so as to form a layer above the nitric acid, and not mix with it. The urine may be introduced from a pipette, or it may be poured from another test-tube by holding both of the tubes in nearly horizontal positions, bringing their mouths together, and then carefully raising their closed ends until the urine quietly flows upon the nitric acid. If albumin is present, there will appear, at the juncture of the liquids, a white zone. If this does not make its appearance at once, the tube should be allowed to stand undisturbed for several minutes in order that traces of the substance may be detected. When urates or urea are present in large quantities, they may give rise, through the action of the nitric acid, to white zones somewhat similar in appearance to that yielded by albumin. These are distinguishable from the zone of coagulated albumin, inasmuch as they are readily dissipated on the application of heat, which should be made in such a manner as not to cause the mixing of the two layers of liquid in the tube. Mucin may likewise cause a white zone, but, as it is not dissolved by heating the liquid, recourse must be had to the test involving the coagulation of albumin by heat, wherein mucin is removed before undertaking the precipitation of the albumin. In making the contact test with nitric acid for albumin, various colors are frequently observed at the line of contact of the urine and acid. These are caused by the action of the nitric acid on the coloring matters of the urine, both normal and abnormal; if albumin is coagulated at the same time the zone may be tinted by these colors. Compare the tests for bile acids given on page 277.

A cold, filtered, saturated, aqueous solution of picric acid is also used to precipitate albumin. It may be applied either by the contact method described under the nitric acid test or by mixing it with the urine to be tested. In the former case a few cubic centimeters of it should be introduced as a layer upon three times its volume of the urine contained in a test-tube, and made to mix with an equal volume of the urine by holding the tube in a slanting position and revolving it until the yellow color extends through the upper half of the tube's contents. The coagulated albumin renders the liquid turbid, the turbidity being more easily discerned by contrast with the clear layer of unmixed urine. When, in consequence of the scantiness of the albumin, the turbidity is very slight, the application of heat to the upper part of the turbid column increases it. After this treatment the tube should be placed aside, that the coagulated albumin may settle; in about an hour or so it will be found as a whitish zone at the line of contact of the liquids. When the plan of mixing the picric acid solution with the urine is adopted, the test is conducted in a similar manner; but of course in this case the coagulated albumin settles to the bottom of the tube. Alkaloids, peptone, and urates are likewise precipitated by picric acid; but their precipitates differ from that of albumin by being dissolved upon the application of heat. Hence, if the test be heated and the coagulum remain undissolved, albumin is indicated.

When it is desired to use mercuric potassium iodide as a reagent for albumin, the decinormal volumetric solution of the compound mentioned on page 197 may be employed. Before applying the test it is best to ascertain whether mucin is present, and, if so, to remove it. This is done by acidulating the urine with acetic acid, and, if a precipitate of mucin forms, filtering. The filtrate, or otherwise clear urine, is then tested with the mercuric potassium iodide solution, either by the contact method or by mixing the reagent with the urine. If the contact method is followed, the reagent is placed in the tube and overlaid with the specifically lighter urine. The coagulated albumin is white. Mercuric potassium iodide precipitates the same interfering substances which picric acid does. In the case of both reagents, the precipitates from these sources dissolve upon heating the test; hence, if this treatment be made and the precipitate persists, it will signify albumin.

The reagent known as acidulated brine is made by adding 35 cubic centimeters of official hydrochloric acid to 500 cubic centimeters of a cold, saturated, aqueous solution of sodium chloride; the precipitate of sodium chloride caused by the addition of the acid is removed by filtration, and the clear liquid preserved for use. This reagent is applied by the contact method, and, because it has a much higher specific gravity than urine, is made the lower layer in the tube. The precipitated albumin which collects in a zone at the juncture of the liquids is white. Alkaloids and peptone do not interfere with this test; mucin, however, does, and, if present, should be removed by adding a drop of hydrochloric acid and filtering before overlaying the acidulated brine. This test is considered to be about equal in delicacy to the nitric acid test, but much less so than the heat test. Its relative value to the latter is sometimes increased by boiling the reagent in the test-tube before covering it with the urine.

The most practical method of estimating albumin in urine is to weigh the precipitate produced by acidifying and boiling the urine. For this purpose, 50 cubic centimeters of the clear urine are mixed with 10 cubic centimeters of official nitric acid, and heated to full boiling. The coagulated albumin is collected on balanced filters by pouring the hot liquid on the same; it is then washed with boiling water until the washings show no more acid reaction to litmus paper, after which it is dried to a constant weight at 100° C. The percentage amount of the albumin is then calculated from the weight of the dry precipitate and that of the urine taken. The amount of albumin usually found in the urine of Bright's disease is less than 0.5 per cent.; as much as 2 per cent. of albumin is very rare.

The practice of roughly estimating albumin by precipitating it in a definite volume of urine, and stating the result in the percentage of the volume through which the precipitate is distributed, is rather confusing, since the result has no relation to the actual percentage by weight.

Peptone.—The occurrence of peptone in urine is called peptonuria; it exists when there is a disintegration of pus-corpuscles somewhere in the body. Peptone differs from albumin in that it is not precipitated by heat, nitric acid, or acidulated brine. It is precipitated by mercuric potassium iodide and picric acid, but the precipitates are redissolved by heating. Peptone may be detected by first adding a few drops of acetic acid to the cold urine and filtering to remove mucin; then boiling the filtrate to coagulate albumin, which is also removed by filtration. The filtrate from this operation is mixed with half its volume of alkaline cupric tartrate volumetric solution. The mixture is filtered to remove the precipitated earthy phosphates, when, if peptone is present, the filtrate will show a rose-colored tint. The foregoing process is a modification of the so-called *biuret test.*

The filtrate from the coagulated albumin may also be tested with picric acid and mercuric potassium iodide; any precipitates which are obtained should be examined by the application of heat, which redissolves the precipitates afforded by peptone.

Bile.—Urine containing bile possesses a yellowish-green, green, greenish-brown, or almost black color. Bilious urine gives a yellow froth on agitation, and stains linen and filter paper yellow.

The principal constituents of bile which are serviceable in its detection are taurocholic acid, $C_{26}H_{45}NSO_7$, and glycocholic acid, $C_{26}H_{43}NO_6$, and a number of peculiar pigments, chief among which are bilirubin, $C_{16}H_{18}N_2O$, and biliverdin, $C_{16}H_{18}N_2O_4$.

The taurocholic and glycocholic acids exist in the form of their sodium salts. The best method of detecting these biliary acids necessitates the separation of their natural salts from the urine. To do this, 100 or 200 cubic centimeters of the urine sample are evaporated to dryness in a dish on a water-bath. The residue is extracted with a few successive portions of absolute alcohol, the alcoholic extractions filtered, and the filtrate mixed with fifteen times its bulk of ether to precipitate the sodium salts of the acids. The ethereal liquid is decanted, the precipitated salts dissolved in distilled water, and the solution decolorized by filtration through animal charcoal.

The resulting colorless fluid is then tested as follows. A single drop of a 20 per cent. solution of cane sugar is added to 5 cubic centimeters of the solution of bile acids contained in a test-tube. Concentrated sulphuric acid is now added, drop by drop, until the precipitate first formed is redissolved ; this may require an equal bulk of the acid, and since the addition of the acid to the aqueous solution causes heat, it is advisable to keep the test-tube in a vessel of cold water, to prevent too great a rise in temperature. The heat should not exceed 70° C. By the time the first precipitate has been redissolved or an equal bulk of sulphuric acid has been added, a cherry-red or purple-violet color should begin to appear, if bile acids are present and the solution is not too cold. No yellow color should appear at this point. If one does appear it indicates that the sugar has been carbonized by the sulphuric acid on account of excessive heat in adding the latter, and the test must be repeated, taking care to keep the temperature down to the degree mentioned.

The most characteristic coloring matter of bile is bilirubin ; it predominates in bilious urine of a saffron-yellow color. Biliverdin and other oxidation products of bilirubin are present in greenish urine. In certain diseases, notably jaundice, these substances exist in the urine in very appreciable amounts.

The coloring matters of bile are detected by the action of fuming nitric acid, which produces a green color with them. The test is made by overlaying some of the acid in a test-tube with an equal bulk of urine. This is done by the directions given under the test for albumin on page 273. If bile pigments are present, a green ring will appear at the juncture of the liquids. Other colors —violet, red, and yellow—may be noticed, whether the green color appears or not ; if the green color is apparent, the other colors will be below it. These colors may be due to normal pigments ; only the green color indicates bile coloring matters. If albumin is present, it will be coagulated by the nitric acid ; in which case the green color will be noticeable in the zone of albumin.

Blood.—Chemically, the presence of blood in urine is detected through the presence of hæmoglobin by what is known as the guaiacum test. This is made by dissolving in alcohol a small particle of guaiacum resin taken from the inner portion of a larger lump. To this solution, in a test-tube, an equal volume of ozonized ether is added ; the latter is made by shaking together in a test-tube equal volumes of official hydrogen dioxide solution and official ether. A small quantity of the suspected urine is then added to the mixture of tincture of guaiacum and ozonized ether, and the mixture shaken. If hæmoglobin is present, a blue color is produced, and is taken up by the ether layer. If the quantity of hæmoglobin is slight, a quarter of an hour may elapse before the color will be visible. The color is not permanent; it soon fades, and in a few hours disappears altogether, leaving the color of the guaiacum solution.

The presence of albumin interferes with the test. On this account, as well as for obtaining additional evidence of the presence of blood, a microscopical examination of the sediment in the urine for the red corpuscles should be made. (See foot-note, page 269.)

Sugar.—The sugars are not normal constituents of urine. The sugar whose presence is sought for most in diagnosis is glucose, $C_6H_{12}O_6$. The occurrence of glucose in urine is known as glycosuria. The passing of such urine indicates the disease called diabetes mellitus, and on that account, in urine analysis, glucose is usually called diabetic sugar. Diabetic urine is usually acid in reaction. Glucose is indicated in urine when the specific gravity is above 1.030, provided the urine is pale in color and the quantity passed in twenty-four hours exceeds 1500 cubic centimeters. While these features are indications, they are by no means conclusive evidence of the presence of sugar; the latter must be found by direct tests, such as are hereafter described.

The detection of glucose by the tests which follow depends upon its oxidation in alkaline solution, or, what involves the same properties, its reducing power under this condition. Since glucose is not the only substance capable of reacting, in the manners to be mentioned, with the reagents, which will be treated of, it follows that none of these are infallible tests for that substance, but that all are subject to more or less interference in results by the presence of other substances. For this reason, it is advisable to employ all of the tests outlined; for while one of them may be rendered useless by the action of some substance other than glucose, another or several of them may be available because unaffected by this substance. The fact that certain drugs and their decomposition products are eliminated by the kidneys renders this course of testing imperative.

Albumin, which is sometimes present in the urine in chronic cases of diabetes, also interferes, to a greater or less degree, with the tests for glucose. Therefore, previous to applying the tests for glucose, it is best to test for albumin. This is done by the means described on page 272. If albumin is found, it should be removed by adding a few drops of official acetic or nitric acid to some of the urine, boiling, and filtering. To remove the earthy phosphates, which, by precipitating in alkaline solution, tend to obscure the tests for glucose, make the filtrate from the coagulated albumin slightly alkaline with official sodium or potassium hydrate solution, warm the mixture gently, until the phosphates separate distinctly, and filter. The following tests are applied to the resulting clear filtrate, which, for convenience, may be designated as *prepared urine*.

Moore's test for glucose is made by adding to 2 or 3 cubic centimeters of the prepared urine half an equal volume of official potassium or sodium hydrate solution, and heating the mixture to boiling. If glucose is present, it is oxidized in the alkaline solution by the oxygen of the atmosphere, the liquid soon acquiring a brownish color, which becomes more intense as the boiling is continued. This color will be deeper the larger the proportion of glucose, becoming almost black if the quantity is very large. The color is said to be due, in the first place, to glucic acid, and finally to melassic acid, both of which are soluble. If an excess of nitric acid be now added to the darkened solution, the brown or black coloration will be discharged, and the odor of caramel will be developed. The odor is often quite pronounced in the alkaline solution before the addition of the nitric acid.

The potassium picrate test consists in adding to about 5 cubic centimeters of the prepared urine about 1 cubic centimeter of a saturated, aqueous solution of picric acid, and about 1 cubic centimeter of official potassium hydrate solution, and boiling for a few minutes. If glucose is present, a dark mahogany-red color, due to potassium picramate, $C_6H_2(NO_2)_2NH_2OK$, the reduction product of potassium picrate, $C_6H_2(NO_2)_3OK$, in alkaline solution, appears; the color is deeper the greater the amount of glucose present. The presence of albumin does not interfere with this test. If normal urine be treated in the same way, it will be darkened somewhat through the action of creatinine on the potassium picrate, but the coloration is not nearly so marked as when sugar is present.

For the bismuth test, a convenient quantity of the prepared urine is mixed with an equal bulk of official potassium or sodium hydrate solution, a very small pinch of bismuth subnitrate added, and the mixture boiled for several minutes. A black precipitate of metallic bismuth results from the reduction of the bismuth oxide, if glucose is present. If only a grayish hue is displayed by the precipitate, the test should be repeated with a smaller quantity of bismuth subnitrate. The quantity of bismuth subnitrate added should be, as near as it is possible to judge, the exact amount which the glucose is capable of reducing. The advantage of adding this quantity is that the yellowish bismuth oxide, which forms from the dehydration of the bismuth hydrate on boiling, will not be present in such quantity as to materially dilute and, consequently, obscure the black color of the metallic bismuth. It may be necessary, in order to obtain a sufficiently small quantity of the bismuth compound for the test, to dissolve some of the salt and add a drop of the solution. In the event of this being required, a small portion of the bismuth subnitrate may be dissolved, by the aid of heat, in the least possible quantity of official nitric acid ; an equal bulk of official acetic acid is added to the resulting solution and the mixture diluted with eight times its volume of water. For use, one drop of this solution is added to the mixture of equal volumes of prepared urine and fixed alkali hydrate solution, and the mixture boiled as described. The evidence of glucose is, of course, the same as when the dry subnitrate is employed. None of the normal constituents of urine are supposed to react with the bismuth test.

Albumin and similar substances containing sulphur, as well as sulphur gases, all of which readily give up their sulphur, must be excluded; otherwise the test may prove deceptive through the precipitation of black bismuth sulphide. The presence of such substances may be established by rendering another portion of the urine alkaline with potassium or sodium hydrate, adding a pinch of lead monoxide, and boiling, when, if such sulphur-containing substances are present, the precipitate will turn black from the presence of lead sulphide.

Trommer's test is made by adding to 5 cubic centimeters of the prepared urine just enough test-solution of copper sulphate to impart a greenish or bluish color, then an equal volume of official potassium or sodium hydrate solution, and boiling the mixture for a minute. If glucose is present, there is produced a yellow precipitate of cuprous hydrate, which, as the boiling is continued, loses water and becomes insoluble, red cuprous oxide. Occasionally the precipitate, instead of turning distinctly red on heating, may remain yellow ; in the absence of interfering substances such a precipitate will be indicative of glucose. A mere change in the color of the mixture to yellow upon heating does not, however, indicate glucose; there must be an actual yellow or red precipitate to show its presence by this test.

As stated on page 192, alkaline cupric tartrate volumetric solution, or Fehling's solution, is also used as a test for glucose, both for qualitative and quantitative purposes. The advantage of Fehling's test over Trommer's test lies in the fact that, in the former, glucose is not depended upon to keep the cupric oxide in solution. Before the reagent is used it should be critically examined, as directed in the place cited.

If the reagent is found to give a precipitate when heated by itself, it must not under any circumstance be used; but, if found to be in perfect condition, it may be employed in the test, which is made as follows. A small quantity of the alkaline cupric tartrate solution is diluted with about four times its volume of water, and heated to boiling. A few drops of the prepared urine are then added, and the boiling continued for a minute. If glucose be present in abundance, as in a decidedly diabetic urine, a yellowish or red opacity or precipitate will be produced. If a negative reaction be obtained, a volume of urine, equal to that of the alkaline cupric tartrate solution taken, is added, and the boiling repeated. If no yellow or red turbidity or precipitate is now visible, the urine is either free from glucose or only very slight traces of the latter are present. To make sure of such small quantities, the tube is set aside for some time in order that any slight precipitate may settle. The cuprous oxide, if any be present, can usually then be seen on the bottom or sides of the tube. If, however, it still fails to be apparent, the liquid is poured through a small filter, to retain any cuprous oxide that may leave the tube; if no precipitate of cuprous oxide is now discernible in either filter or tube, the inner surface of the test-tube is wiped with a pellet of cotton attached to the end of a glass rod, for the purpose of collecting any widely separated particles of cuprous oxide and bringing them to view. If cuprous oxide cannot be found by these means, it certainly can be safely said that glucose is absent.

In applying the test under consideration, a green turbidity is sometimes encountered. This is ascribed to the presence of a large amount of creatinine in the urine, and in such cases creatinine is said to have the power of preventing the precipitation of cuprous oxide by glucose.

If, on account of the behavior of interfering substances, the foregoing tests are exhausted without the analyst being able to reach a decision regarding the absence or presence of glucose, any of the latter substance which may be present can be isolated by the following process, and the tests applied to the purified substance. 50 cubic centimeters of the urine are mixed with 60 cubic centimeters of a 10 per cent. solution of neutral lead acetate. The mixture is filtered, the precipitate drained and washed, and the filtrate and washings treated with an excess of ammonium hydrate and more lead acetate, unless an excess of the latter has been already used. The precipitate produced will contain any glucose present, in the form of a combination with lead oxide. This precipitate is collected on a filter and washed with cold, distilled water until the excess of alkali is removed, litmus paper being used to determine this matter. If the precipitate is very bulky it may be more conveniently washed by subsidence and decantation. The properly washed precipitate is suspended in about 100 cubic centimeters of distilled water, and decomposed by passing into the mixture a stream of hydrogen sulphide until the insoluble matter is uniformly blackened and the gas is in decided excess. The lead sulphide is then collected on as small a filter as will accommodate it, the filter being supported by a funnel placed in the mouth of a graduated cylinder. The precipitate is allowed to drain thoroughly, and is afterwards washed with small successive portions of warm distilled water until the filtrate and washings measure about 125 cubic centimeters. This liquid contains the glucose, and is evaporated in a dish on a water-bath to expel the excess of hydrogen sulphide and reduce the volume of the liquid to that of the portion of urine taken. To attain the latter end with the least expenditure of time and trouble, the liquid may be evaporated to about 25 cubic centimeters, then allowed to cool, and afterwards poured into a graduated cylinder, in which it is made up to 50 cubic centimeters by the addition of successive portions of water, previously used to rinse the dish. The solution of glucose prepared in this manner is equal in strength to the original urine, and may be subjected to the qualitative tests for the detection of the substance, usually without interference.

The usual method of estimating glucose in urine is by means of alkaline cupric tartrate volumetric solution. The reagent must be tested by itself according to the directions given on page 193 before it is used; see also the qualitative test on page 281. The estimation may be conducted both volumetrically and gravimetrically. The former plan is the one most frequently pursued in urine analysis. Both methods require the removal of earthy phosphates and of any albumin which may be present; the separation of these substances may be conducted by the directions given on page 279. If for any reason it is necessary to separate the glucose from the urine, the method already outlined for that purpose may be resorted to; the final solution of glucose is fit for both methods of determination. For the volumetric process, 50 cubic centimeters of the urine are freed from albumin (if necessary) and earthy phosphates; the precipitate of albumin is washed with hot distilled water until the acidity is entirely washed into the filtrate; the precipitate of earthy phosphates is washed with hot distilled water until the alkalinity is completely washed into the filtrate; the filtrates are collected in a graduated cylinder. The tests for acidity and alkalinity are to be made with litmus paper, moistened with distilled water by bringing it into contact with a drop of the washings at the end of the funnel. If tolerably small filters are used, and, after the liquids have passed through, they are allowed to drain before the wash-water is applied, the washing of both filters may usually be accomplished by the use of 50 cubic centimeters of hot water; thus making 100 cubic centimeters of prepared urine. In any case, the filtrate and washings are allowed to cool to the ordinary temperature, and are then made up to a definite volume by the addition of distilled water of the temperature of the room. The liquid is then thoroughly mixed by inverting the stoppered cylinder several times. A burette is then filled with it, and the titration of the alkaline cupric tartrate volumetric solution conducted in the manner described on page 194. When the volume of the diluted urine necessary to decolorize 10 cubic centimeters of the reagent is finally found, the degree of dilution must be considered, in order to ascertain how many cubic centimeters of the original urine are present in that volume. Suppose, for example, the 50 cubic centimeters of original urine are made up to 100 cubic centimeters, and that 16 cubic centimeters of the dilution are required for the decoloration of 10 cubic centimeters of the alkaline cupric tartrate solution; then 8 cubic centimeters of the original urine must contain the 0.050 gramme of anhydrous glucose required to reduce the cupric oxide of 10 cubic centimeters of the reagent. To find the percentage amount of anhydrous glucose present, the weight of the 8 cubic centimeters must be known. Since the weight of a liquid in grammes can be found by multiplying its volume in cubic centimeters, measured at a given temperature, by its specific gravity at the same temperature, it follows that, if we assume the specific gravity of the urine in question to be 1.030, the 8 cubic centimeters will weigh 8.240 grammes. Knowing the weight of the material taken for analysis and the weight of the substance contained in it, the percentage amount of that substance is found by proportion as follows:

8.240 gm. : 0.050 gm. :: 100 per cent. : 0.66 per cent.

When more accurate results than are obtainable by the volumetric method are desired, recourse must be had to the gravimetric process. In this, 10 or 25 cubic centimeters of the urine are taken for the estimation, according as the qualitative test with alkaline cupric tartrate solution shows much or little glucose. The precipitates of albumin and earthy phosphates are thoroughly washed, as directed in the volumetric process, but it is not necessary to allow the prepared urine to cool, and to determine its volume, unless duplicate estimations are to be made on aliquot parts of the prepared urine. The portion of the prepared urine to be treated is mixed in a beaker with about 25 cubic centimeters of alkaline cupric tartrate volumetric solution, or enough of the latter to impart a decided blue color. The beaker is then placed in a water-bath which has been heated nearly to boiling; the bath is then brought to the boiling point, and the beaker allowed to remain at the boiling temperature for 20 minutes, or until the precipitate of red cuprous oxide has fully settled. The blue color of the reagent, indicating an excess of the latter, must be distinctly visible in the fluid at this point. On account of the turbidity of the beaker's contents it is often necessary, in order to decide the presence or absence of the blue color of the reagent, to remove the beaker from the water-bath, and, holding it in a slanting position, to look through the edge of the liquid towards the light. If the blue color has disappeared, another addition of the reagent, in sufficient quantity to insure an excess, may be made, and the heating in the water-bath continued until the precipitate has subsided; but it will be found more accurate to commence the estimation again, adding the entire quantity of alkaline cupric tartrate solution required at one time. When an excess of the reagent is found in the solution after heating in the manner described, and the precipitate has settled, the liquid is decanted upon a Swedish filter, and the cuprous oxide finally transferred to the same, the last portions being collected from the sides and bottom of the beaker by means of a glass rod tipped with a short section of rubber tubing. The filter and cuprous oxide are thoroughly washed with hot water until all greenish or bluish color of soluble copper salts, and all alkalinity, due to potassium hydrate, are removed from the paper and precipitate ; litmus paper is used to determine the last condition. The properly washed precipitate is then thoroughly dried in an air-bath at about 100°. Since cuprous oxide is subject to oxidation by drying, it is best to completely convert it by ignition into cupric oxide, and weigh it in that form. If there is much of the cuprous oxide, it may now be separated from the filter, the latter burned as described on page 76, and the cuprous oxide and filter ash then intensely ignited in a weighed porcelain crucible until a constant weight is attained. When the amount of cuprous oxide is too small to permit its separation from the filter, the latter may be folded about the former, the whole put into a weighed porcelain crucible, and intensely ignited. The cupric oxide produced in the ignition is black ; it results from oxidation of the cuprous oxide by the oxygen of the air, under the influence of heat. A second ignition and weighing will be needed to prove that the cuprous oxide is completely changed to cupric oxide. The ignitions should be of about 10 minutes' duration, and the crucible and cupric oxide should be allowed to cool in a desiccator before they are weighed.

The weight of anhydrous glucose contained in the portion of urine used for the estimation is found by taking 45.38 per cent. of the weight of the cupric oxide. This factor is derived from the relation of the quantities of glucose and cupric oxide which take part in the reduction of the alkaline cupric tartrate solution, as explained on page 192. To find the percentage amount of anhydrous glucose present in the urine, employ a proportion of the kind given on page 284 for the calculation of the percentage result of the volumetric estimation.

Ammonium Carbonate.—When successive, freshly voided portions of urine are uninterruptedly alkaline in reaction, the condition may be due to the conversion, within the bladder, of urea, through the absorption of water, into ammonium carbonate. The ammonium carbonate is recognized by the ammoniacal odor of the urine, and by the effervescence produced upon adding a drop of hydrochloric acid to a portion of the specimen. The foregoing statement applies only under the conditions named, since all urines, upon standing, eventually develop ammonium carbonate through the same process.

CHAPTER III.

ANALYSIS OF URINARY CALCULI.

THE three varieties of calculus or gravel most common are uric acid and its compounds, calcium oxalate, and the mixed phosphates. Calculi of calcium carbonate, xanthine, cystine, and urostealith occur, though very rarely.

Uric acid calculi are red or brownish red, and usually smooth, but sometimes tuberculated. Calcium oxalate calculi are usually dark brown or dark gray in color, hard, and rough; when small they are sometimes smooth. The tuberculated variety is known as mulberry calculus, the smooth variety as hemp-seed calculus. The calculus of mixed phosphates, known also as fusible calculus, is composed of calcium phosphate and magnesium ammonium phosphate. Such calculi are white, brittle, and fusible before the blowpipe. Calculi of pure calcium phosphate are rare; they are called bone-earth calculi. There is also an uncommon calculus consisting entirely of magnesium ammonium phosphate; it is referred to as triple phosphate calculus.

Large calculi are frequently composed of several substances. In such cases the constituents are usually arranged in concentric layers about a nucleus. The nucleus may be inorganic or organic matter; of the former, calcium oxalate is the most frequently occurring, while blood-clots are very often the organic matter present. Since the layers may be of different composition, the calculus should be powdered, and the powder thoroughly mixed, before undertaking an analysis of it.

The following scheme will serve for determining the composition of simple calculi:

Heat a small portion of the powdered calculus on platinum foil to redness,—

I. It is completely consumed. To another portion of the powdered calculus apply the murexide test. (See page 269.)

  A. A purple color is obtained. Treat a portion of the original powder in the cold with KOH solution, and hold a piece of moistened red litmus paper over the test,—

  - *a.* A blue coloration of the paper indicates *ammonium urate.*
  - *b.* No blue coloration : *uric acid.*
- *B.* No purple color is obtained.
  - *a.* But the HNO_3 leaves on evaporation a yellow residue, which becomes reddish yellow on the addition of KOH : *xanthine.*
  - *b.* The HNO_3 solution acquires a dark-brown color, and on evaporation leaves a residue soluble in NH_4OH : *cystine.* Confirm by testing original powder. Cystine is soluble in NH_4OH, and deposits, when allowed to evaporate spontaneously, hexagonal plates. When heated, cystine gives off the odor of CS_2.
  - *c.* Not belonging to the foregoing divisions. Soft when fresh ; dark brown and brittle when dry ; softens on warming ; soluble in ether : *urostealith.*

II. A residue remains. To another portion of the powdered calculus apply the murexide test. (See page 269.)

- *A.* A purple color is obtained : *urates.*
  - *a.* The powder fused during the heating. Bring some of it into the flame on platinum wire,—
    1. It colors the flame yellow : *sodium urate.*
    2. It colors the flame violet : *potassium urate.*
  - *b.* The powder did not fuse during the heating. Dissolve the residue left upon ignition in dilute HCl, add NH_4OH in excess, and then add $(NH_4)_2C_2O_4$,—
    1. A white precipitate : *calcium urate.*
    2. No precipitate : *magnesium urate.* Confirm by producing a white, crystalline precipitate in the solution by adding Na_2HPO_4 and stirring.

- *B.* No purple color is obtained. Heat a portion of the powdered calculus before the blow-pipe on platinum foil,—
  - *a.* It fuses. Dissolve the residue in warm acetic acid, dilute with water, and add $(NH_4)_2C_2O_4$.
    1. A white precipitate: *calcium phosphate.*
    2. No white precipitate: *magnesium ammonium phosphate.* Confirm by making alkaline with NH_4OH and stirring well; the confirmation is a white, crystalline precipitate.
  - *b.* It does not fuse. Test the reaction of the residue with moistened litmus paper.
    1. The reaction is not alkaline. Dissolve the residue in HCl, and add NH_4OH in excess; a white, gelatinous precipitate: *calcium phosphate.*
    2. The reaction is alkaline. Treat some of the powdered, original calculus with HCl.
       - *α.* It dissolves with effervescence: *calcium carbonate.*
       - *β.* It dissolves without effervescence: *calcium oxalate.*

PART V.

SPECIAL PROCESSES.

CHAPTER I.

WATER ANALYSIS.

COLLECTION OF SAMPLE.

EVERY care should be taken in collecting the sample of water for analysis to secure a truly representative specimen of the supply and to avoid introduction of foreign matters. The five-pint glass-stoppered bottles used for containing acids are suitable for holding the sample; only glass-stoppered bottles should be used for the purpose. Five pints of the water will usually suffice for most sanitary and technical examinations; if a more detailed analysis is required, of course a larger quantity must be taken.

In collecting from a well, river, or tank, plunge the bottle itself, if possible, below the surface; but if an intermediate vessel must be used, see that it is thoroughly clean and well rinsed with the water. Avoid the surface water and also any deposit at the bottom.

If the sample is taken from a pump or tap, take care before collecting to pump off or run off the water which has been standing in the pump or pipe, then allow the stream to flow directly into the bottle. If it is to represent a town water-supply, take it from the service-pipe communicating directly with the street main.

In every case first fill the bottle completely with the water, thus expelling all gases and vapors, empty it again, rinse once or twice carefully with the water, then fill it nearly to the stopper, and tie down the latter tightly.

At the time of collection note the source of the sample, whether from a deep or shallow well, a river or spring, and also its local name, so that it may be clearly identified.

If it is from a well, ascertain the nature of the soil, subsoil, and water-bearing stratum; the depth and diameter of the well, its distance from neighboring stables, cesspools, drains, factories, or other possible sources of pollution; whether it passes through an impervious stratum before entering the water-bearing stratum, and, if so, whether the sides of the well above this are or are not water-tight.

If it is from a river, ascertain the distance from the source to the point of collection; whether any pollution takes place above that point, and the geological nature of the district through which it flows.

If it is from a spring, take note of the stratum from which it issues.

The sample should be kept in the dark, and analyzed with as little delay as possible.

PRELIMINARY EXAMINATION.

The color of the water should be observed as seen in a tall, narrow, colorless glass tube, standing upon a white surface. It may be compared with distilled water in a similar vessel. A drinking water should be colorless. The odor may be ascertained by putting about 150 c.c. of the water into a clean, wide-mouthed bottle of about 250 c.c. capacity, inserting the stopper, and warming in the water-bath to 40° C.; when this temperature is reached, the bottle is removed from the water-bath, vigorously shaken, the stopper removed, and the odor of the water noted. The stopper may be replaced and the test repeated. A water to be fit for drinking purposes should have an agreeable taste, neither flat, salty, nor sweetish; nor should the odor be such as to cause aversion. But a water which is clear, colorless, odorless, and tasteless may be highly contaminated with dangerous substances; hence the necessity of analysis. Ordinary drinking water should be neutral to litmus. If an acid reaction is observed, the water should be boiled in order to determine if the reaction is due to carbonic acid; if so, the wine-red color will disappear. The presence of other acids would, of course, unfit a water for drinking purposes and for many technical applications, especially for use in boilers.

Before commencing the quantitative analysis, it is necessary to decide whether the water shall be filtered or not before analysis. This must depend on the purpose for which the examination is undertaken. When required, the determination of the suspended matter is done by filtering a liter of the sample through a dried and weighed filter. The paper of this filter must be entirely free from soluble matter. After the liquid has passed through, the filter and its contents are dried at 110° C., and weighed. The gain in weight over that of the filter is the weight of suspended matter in a liter of water.

The amounts of the substances estimated in a water analysis are almost invariably stated in terms of parts per million, which is equivalent to the number of milligrammes of a substance in one liter. Thus, if one liter of the water held 0.005 gramme of solids in suspension, the amount would be given in the statement of analysis as 5 parts per million. Occasionally the results are desired in grains per gallon. If the parts per million be multiplied by .058, the product will be the grains per United States gallon; if multiplied by .07, it will indicate grains per imperial gallon.

TOTAL SOLIDS.

As a general rule, where the suspended matter is to be determined, the water is filtered before the estimations of the nitrogen and the total soluble solids are undertaken; under other circumstances, it should merely be well mixed before taking the portion for analysis. In the analysis of waters intended for drinking, mere traces of suspended matter are removed by filtration, as already described, on the assumption that these insoluble substances will be separated previous to drinking the water.

For the determination of the total dissolved solids, 250 c.c. of the clear water are evaporated in a weighed platinum or porcelain dish. A dish of about 100 c.c. capacity is a convenient size. To prevent loss through bumping or accidental boiling, the evaporation should be done on a water-bath. The residue must be brought to a constant weight.

After the weight of the residue is obtained, the dish should be cautiously heated to low redness, and the effect noted. If organic matter is present, it is at first charred, and by continued heating burned off. The organic matter, under the influence of heat, not infrequently develops odors which indicate its character and source. In water nearly or quite free from organic matters, the residue on igniting will give no appreciable blackening or odor. On account of the fact that certain of the inorganic salts are decomposed by ignition, with loss of water of crystallization or of their acid radicals, the *loss on ignition* cannot be taken as a measure of the organic matter present in the water; but the possible charring is an important matter to be observed.

The fixed inorganic solids may be analyzed in the usual way for bases and acids; or, if preferred, another portion of the water may be evaporated and the residue examined without ignition. Poisonous metals may be looked for in the unevaporated water, or in the residue of evaporation, by applying the usual tests. If required, a full quantitative analysis of the mineral constituents of the residue may be made.

CHLORINE.

Unless the source of the water is situated near a body of salt water, or in a stratum known to contain chlorides, the presence of any notable quantity of chlorine is regarded as evidence of sewage contamination, chlorine being a normal constituent of urine. It is not the chlorine, or chlorides in which the element is contained, that are objected to, but the organic matters which are likely to accompany it. (See also Phosphates, page 298.)

To determine the chlorine, place 100 c.c. of the water in a beaker, add a few drops of potassium chromate test-solution, and carefully run in decinormal silver nitrate volumetric solution from a burette until a slight red tint remains permanent on stirring. Each c.c. of the solution represents 0.003537 gm. of chlorine.

The water must be neutral for titration; if acid, stir in a very small quantity of pure calcium carbonate; if alkaline, acidify slightly with nitric acid, then add calcium carbonate.

If, on account of the small quantity of the chlorine, the water needs to be concentrated before undertaking the titration, a slight excess of pure sodium carbonate may be added. In such cases the chlorine in the concentrated water may be estimated also by the gravimetric method described on page 112.

NITROGEN IN AMMONIUM COMPOUNDS AND IN ORGANIC MATTER.

Ammonia is one of the first products in the putrefaction of nitrogenous organic matter; it is also produced in the artificial oxidation of such substances. The recognition of ammonia, pre-existing or artificially produced by oxidation, may, then, be used as a means of detecting the presence of nitrogenous matter, or of establishing the fact that such matter has decayed in contact with the water. Hence the determination of the nitrogen existing in the water in the form of ammonium compounds and in organic matter is an important feature in the sanitary examination of water.

The following reagents are required:

Nessler's Reagent.—Dissolve 35 gm. of potassium iodide in 100 c.c. of water. Dissolve 17 gm. of mercuric chloride in 300 c.c. of water. Solution may be aided by heat, but the liquids must be cooled before use. Add the mercuric chloride solution to that of the potassium iodide until a permanent precipitate is produced. Then dilute with a 20 per cent. solution of sodium hydroxide to 1000 c.c., and add mercuric chloride solution until a permanent precipitate again forms; allow the mixture to stand until the precipitate settles, then decant the clear solution as it is needed for use. The reagent improves with age. It is conveniently applied from a pipette, which is graduated to deliver 2 c.c.

Traces of ammonia or ammonium compounds are detected by Nessler's reagent; a yellow, yellowish-brown, or reddish-brown color or precipitate is obtained when free ammonia or ammonium salts are present. The color reaches its full depth in five minutes.

Sodium Carbonate Solution.—Fifty gm. of pure sodium carbonate are intensely heated, dissolved in 250 c.c. of distilled water, and the solution boiled down to 200 c.c.

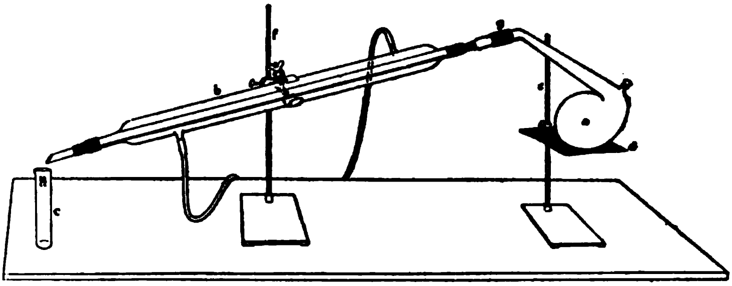
Ammonium-Free Water.—If the distilled water of the laboratory gives a reaction with Nessler's reagent, it should be treated with sodium carbonate, about one gramme to the liter, and boiled until about one-fourth has been evaporated. Ammonium-free water may also be obtained by distilling, in a retort, water made slightly acid with sulphuric acid. Since the distilling apparatus is likely to yield ammonia, successive portions of the distillate must be tested with Nessler's reagent and rejected, until no more evidence is obtained, before collecting the water for use.

Standard Ammonium Chloride Solution.—Dissolve 0.381 gm. of dry, pure ammonium chloride in 100 c.c. of ammonium-free water. For use, dilute 1 c.c. of this solution with pure water to 100 c.c. 1 c.c. of this dilute solution contains 0.00001 gm. of nitrogen.

Alkaline Potassium Permanganate Solution.—Dissolve 200 gm. of stick potassium hydroxide and 8 gm. of potassium permanganate in a liter of distilled water. Boil the solution until about one-fourth is evaporated, then make up to a liter with ammonium-free water. Determine the amount of ammonia which the solution still contains by distilling 50 c.c. of it with 500 c.c. of ammonium-free water, according to the directions given for the estimation of the ammonia in water. The ammonia found must be deducted from the results of each analysis in which this reagent is used.

The distilling apparatus shown in Fig. 16 is required for the analytical process. Half a dozen or more of the graduated cylinders represented by *c* in the cut should be at hand. These cylinders should be about 2.5 cm. in diameter, and graduated to hold 50 c.c.; they should be made of colorless glass.

Fig. 16.



The tubulated glass retort, *a*, should have a capacity of about 1000 c.c. The neck of the retort should be bent at the end so that it can be arranged as shown in the figure. The retort is supported on a ring over which a wire gauze, *d*, is put. Heat is applied to the retort by means of a Bunsen burner placed on the base of the retort stand, *e*. A section of rubber tubing, *g*, is used to make a tight joint between the neck of the retort and the condenser tube. During the distillation, a rapid circulation of water should be maintained through the condenser, *b*.

The estimation of the nitrogen in the ammonium compounds and in organic matters is begun by freeing the apparatus from ammonia. This is done by filling the retort half full of water from the laboratory supply, and distilling until the water that is collected in the receiving cylinder gives no color with Nessler's reagent.

When this condition is attained the flame is withdrawn and the retort disconnected and emptied of any remaining water. The retort is then rinsed with a little of the water to be analyzed. 500 c.c. of the sample are then poured in through the tubulure, the retort stoppered, replaced in position on the wire gauze, and attached to the condenser. About 5 c.c. of the sodium carbonate solution are then added, and a cylinder, which has been rinsed perfectly clean with ammonium-free water, placed to receive the distillate. These arrangements being complete, the contents of the retort are heated to boiling. When 50 c.c. of distillate have collected in the cylinder, the latter is removed and another of these vessels put in its place. 2 c.c. of Nessler's reagent are then added to the 50 c.c. of distillate. If the reagent is delivered from a pipette, the test will need no further mixing. A yellow or yellowish-brown color or precipitate is produced, the intensity of the color being directly proportional to the amount of ammonia present. The color reaches its full depth in five minutes. The amount of ammonia causing this color is to be found by matching the color. The color is matched by putting into another cylinder 50 c.c. of ammonium-free water, some of the standard ammonium chloride solution, and 2 c.c. of Nessler's reagent. If the color produced by this trial is lighter or darker than that of the Nesslerized distillate, other comparison tests are made by using larger or smaller amounts of the ammonium chloride solution, until the color is exactly matched.* It is hardly necessary to say that these tests should be made in an atmosphere free from ammonia.

The distillation is continued, the successive portions of 50 c.c. of distillate tested with Nessler's reagent, and any resulting colors matched, as before. When the distillate no longer produces a color with Nessler's reagent, the flame is removed. The quantity of nitrogen in the ammonium chloride solution required to match the colors of the distillates is noted ; it represents the *free ammonia* in 500 c.c. of the water. By doubling the nitrogen which this volume contains the *free ammonia* in 1000 c.c. of the water is found ; this amount in milligrammes gives the parts per million.

As a general thing the greater part of the free ammonia will be obtained in the first 50 c.c. of distillate. Sometimes, however, the amount of the ammonia increases with the successive distillates.

When the distillate ceases to show a color with Nessler's reagent, as already stated, or when the ammonia is found to be increasing with the continuance of the process, 50 c.c. of alkaline potassium permanganate solution are added to the contents of the retort, and the distillation started again. The distillate is collected in portions of 50 c.c., as before. These portions are treated with Nessler's reagent, and the colors matched as in the case of the free ammonia. The nitrogen of the ammonium chloride solution required for this purpose is noted. From the total nitrogen found at this stage of the operation that yielded by 50 c.c. of the alkaline potassium permanganate is deducted; the difference is due to the ***albuminoid ammonia*** of the 500 c.c. of water.

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* This method of estimating substances is known as *colorimetric analysis*, and, as can be readily seen, is applicable to many substances which yield distinctive color reactions in the wet way.

Since the potassium permanganate is reduced by the organic matter, it might appear that, in the absence of inorganic reducing substances, such as nitrites, ferrous compounds, and sulphides, the amount of the salt reduced could be taken as a measure of the organic matter present. It will be seen from the tests of the United States Pharmacopœia, given on pages 302 and 303, that such use may be made of the permanganate.

NITROGEN AS NITRATES.

Nitrates result from the complete oxidation of nitrogenous organic matter. All natural waters are liable to contain nitrates, and especially the water of deep wells. A water which contains a large amount of mineral matter but no nitrates is likely to be contaminated by some reducing agent, such as sewage, which has destroyed the nitrates obtained from the soil.

The reagents required for the detection and estimation of nitrogen as nitrates are:

Phenoldisulphonic Acid.—Mix strong sulphuric acid and pure phenol in the proportion of 37 gm. of the former to 3 gm. of the latter, and heat the mixture for six hours in the water-bath, having the flask in contact with the boiling water.

If the phenoldisulphonic acid solidifies upon cooling, it can be easily liquefied for use by the application of a gentle heat with the water-bath.

Standard Potassium Nitrate Solution.—Heat about 1 gm. of pure potassium nitrate just sufficiently to fuse it, then allow it to cool, and weigh off 0.720 gm. Dissolve this in enough pure water to make 1000 c.c. Each c.c. of this solution contains 0.0001 gm. of nitrogen as nitrate.

To detect the nitrates, evaporate 100 c.c. of the water just to dryness in a porcelain dish, add exactly 1 c.c. of the phenoldisulphonic acid, and mix thoroughly by stirring with a glass rod. Then dilute the mixture with about 25 c.c. of water, add ammonium hydrate in excess, make the solution up to 50 c.c. with water in a graduated cylinder, and mix well.

If nitrates are present, a yellow color is produced by the action of the liberated nitric acid on the phenol; this color, due to nitrophenols, is rendered darker by the excess of ammonia water.

To match the color for estimation of the nitrates, evaporate in a dish 1 c.c. of the standard potassium nitrate solution just to dryness, add exactly 1 c.c. of phenoldisulphonic acid, mix well with a glass rod, dilute with water, and add ammonium hydrate in excess, as before, finally bringing the volume of the well mixed liquid to 50 c.c. by the addition of pure water. Compare the colors of the two solutions, and dilute one of the liquids, if necessary, until the colors agree in intensity. From the quantities of water and potassium nitrate solution used and the data of dilution calculate the amount of *nitrogen present as nitrates.*

NITROGEN AS NITRITES.

Nitrites are present in water as the result either of incomplete nitrification of ammonia or the reduction of pre-existing nitrates, under the influence of reducing agents or microbes. Since they are intermediate products, their presence in water is usually evidence of existing fermentative changes, although they may be present because oxygen is not available for their conversion into nitrates. The latter is sometimes the case in deep waters in which fermentative changes have long since ceased.

The following solutions are used in the detection and estimation of nitrites:

Sulphanilic Acid Solution.—Dissolve 0.5 gm. of sulphanilic acid (para-amidobenzenesulphonic acid) in 150 c.c. of diluted acetic acid, sp. gr. 1.04.

Naphthylamine Acetate Solution.—Boil 0.1 gm. of solid naphthylamine (α-amido-naphthalene) in 20 c.c. of water, filter the solution through a plug of washed absorbent cotton, and make the filtrate up to 200 c.c. with diluted acetic acid. The solution should be colorless.

Standard Sodium Nitrite Solution.—Dissolve 0.274 gm. of pure silver nitrite in pure water, and add a dilute solution of pure sodium chloride until a precipitate ceases to form. Then dilute with pure water to 250 c.c. and allow to settle clear. For use, dilute 10 c.c. of the clear solution to 100 c.c. One c.c. of the dilute solution is equivalent to 0.00001 gramme of nitrogen.

Nitrites are tested for by adding to 50 c.c. of the water contained in one of the color comparison cylinders 4 c.c. each of the solutions of sulphanilic acid and naphthylamine acetate. The reagents are added by means of separate pipettes. In the presence of nitrites a pink color is rapidly developed. If such a color is obtained, the amount of nitrogen present as nitrite is estimated by placing 1 c.c. of the standard sodium nitrite solution in one of the comparison cylinders, adding nitrite-free water up to 50 c.c., and treating with the reagents as in the case of the water. The colors of the liquids in the cylinders are then exactly matched by diluting a definite quantity of the well-mixed, darker solution. From the quantity of standard sodium nitrite solution required to equal the color yielded by the water the amount of *nitrogen as nitrites* present in the water is calculated.

PHOSPHATES.

Since phosphates, like chlorides, are normal constituents of urine, the presence of the former in water will sometimes indicate sewage contamination where the indication through chlorides cannot be relied upon, as, for instance, in water from near the sea-coast or from salt regions. The absence of phosphates affords no positive proof of freedom from contamination, however, since the phosphates of the sewage may be rendered insoluble during their filtration through the soil.

The phosphates are detected and estimated by acidifying 500 c.c. of the water with nitric acid, and evaporating the liquid to 25 c.c. The phosphorus pentoxide is then precipitated with ammonium molybdate as described on page 122. Instead of converting the ammonium phosphomolybdate into magnesium pyrophosphate for weighing, it is usually, in water analysis, collected on a small weighed filter, washed till the adhering acid is removed, dried at 40° C., and weighed. From its weight the amount of PO_4 present is calculated. This is found by multiplying the weight of the dried precipitate by 0.05.

HARDNESS.

When calcium and magnesium salts are present in a water, they form insoluble precipitates with soap, which are inconvenient in washing; such a water is called hard, and requires the use of a great deal more soap in order to produce a lather. These salts are usually sulphates or carbonates, frequently both, the latter being held in solution by the carbon dioxide present. When the hardness is due to sulphate, the water is said to be *permanently* *hard*, in distinction from that which contains carbonates held in solution by carbon dioxide, which is termed *temporarily hard*. In the latter case it becomes a soft water by simple boiling, which drives off the carbon dioxide and precipitates the salts as carbonates. Water is said to have one degree of hardness when it contains one part of calcium carbonate, or its equivalent, in 100,000 parts. "Each degree of hardness indicates the destruction and waste of twelve parts of the best hard soap by one hundred thousand parts of water" (Frankland). The examination of hardness is also an important matter in the analysis of a water intended for boiler purposes, since the scale-forming ingredients of a water are usually composed of calcium and magnesium carbonates and calcium sulphate.

The degree of hardness is sometimes determined by agitating the sample of water with a standard solution of soap until a permanent lather is produced. But the method in more general use at the present time dispenses with the use of soap, and employs, instead, sodium carbonate and sulphuric acid volumetric solutions.

To determine *temporary hardness*, put 100 c.c. of the water in a dish, add a few drops of lacmoid solution as indicator, heat the liquid to boiling, and carefully titrate with fiftieth-normal sulphuric acid volumetric solution until a red color is produced. Each cubic centimeter of acid required will represent one part of calcium carbonate, or its equivalent, per 100,000 parts of the water; in other words, one degree of hardness.

The *permanent hardness* is ascertained by taking 100 c.c. of the water and adding to it a rather large known excess of fiftieth-normal sodium carbonate volumetric solution. The quantity must be sufficient to decompose all of the permanently soluble calcium and magnesium salts present; as a rule, a volume equal to the water taken will be more than sufficient for the said purpose. The mixture is evaporated to dryness in a nickel or platinum dish, and the soluble portion of the residue removed by treatment with successive small portions of distilled water. The solutions so obtained are filtered through a very small filter, which is afterwards washed. The mixed filtrate and washings are tinted with lacmoid solution, heated to boiling, and titrated while hot with the fiftieth-normal sulphuric acid volumetric solution. The difference between the number of cubic centimeters of fiftieth-normal sodium carbonate volumetric solution added, and the volume of fiftieth-normal sulphuric acid volumetric solution required for the soluble matters of the residue, gives the permanent hardness, each cubic centimeter of the sodium carbonate solution required being equal to one part of calcium carbonate, or its equivalent, per 100,000 parts of the water.

Some waters contain alkaline carbonates; in such cases there is no permanent hardness, because the salts to which this is due are decomposed by the alkaline carbonates with precipitation of those bases which form insoluble soaps. In examining a water of this kind the temporary hardness will appear greater than it really is, on account of the alkaline carbonate neutralizing the volumetric acid solution, and the estimation for permanent hardness will show more sodium carbonate than was actually added. The excess in the latter case is the amount of alkaline carbonate originally present in the water; and, if the volume of fiftieth-normal sulphuric acid volumetric solution required to neutralize it at this point be deducted from the volume of the acid volumetric solution used in the determination of the apparent temporary hardness, the difference will be the volume of acid needed for the real temporary hardness. The alkaline carbonate originally present is calculated into sodium carbonate.

CARBON DIOXIDE.

The following method is adapted to the estimation of carbon dioxide in such waters as are likely to be used for technical purposes:

100 c.c. of the water are put into a flask with 3 c.c. of a strong, neutral solution of barium chloride, and 2 c.c. of saturated solution of ammonium chloride; 45 c.c. of decinormal barium hydrate volumetric solution are then added, the flask stoppered, its contents shaken, and put aside to settle. When the precipitate has fully subsided, 50 c.c. of the clear liquid are removed by means of a pipette, and titrated with decinormal acid. The quantity of acid required must be multiplied by 3 for the total barium hydrate solution added to the 100 c.c. of water; the number of c.c. so found must be deducted from 45, the number of c.c. of decinormal barium hydrate solution used; the remainder is the number of c.c. of decinormal barium hydrate volumetric solution required for the carbon dioxide of 100 c.c. of water, in excess of that existing as normal carbonates. Each c.c. of decinormal barium hydrate volumetric solution is equivalent to 0.002199 gm. of carbon dioxide.

HYDROGEN SULPHIDE.

The estimation of hydrogen sulphide is sometimes required in the analysis of mineral waters and waters intended for technical purposes. It is objectionable in waters to be used in boilers and for laundry purposes, since the hydrogen sulphide is liable to change by oxidation to sulphate, and thus contribute to the scale-forming and soap-destroying properties of the water.

Hydrogen sulphide may be estimated by the following process. 10 c.c., or any other necessary volume of centinormal iodine volumetric solution, are measured into a 500 c.c. flask, and the water to be examined added until the color of the iodine disappears. 5 c.c. of starch test-solution are then added, and the mixture titrated with centinormal iodine volumetric solution until a permanent blue color is established. The flask is then filled to the mark with pure distilled water. By deducting the sum of the volumes of iodine solution, starch solution, and pure water used from 500 c.c., the volume of the water sample operated on is found. A correction should be made for the volume of iodine solution required to impart the color. This volume is found by diluting 5 c.c. of the starch test-solution to 500 c.c. with pure distilled water, and running in centinormal iodine volumetric solution until the color of the liquid containing the water to be tested is matched. The volume of iodine solution so required is deducted from that used in the experiment with the sample of water. The difference is that actually needed to oxidize the hydrogen sulphide of the water taken. One c.c. of centinormal iodine volumetric solution is equivalent to 0.0001699 gm. of hydrogen sulphide.

CONCLUSIONS AS TO QUALITY.

No definite rule can be laid down by which to judge the results of all water analyses ; much must be left to the judgment of the analyst and to the special information he may have regarding the source of the water and other matters throwing light upon its possible composition. Besides what has already been said regarding the properties of a water fit for drinking, the following quantities of some of the substances for which methods of estimation have been given may usually be taken as the maximum amounts of these substances allowable. These limits have been fixed by sanitary authorities :

Total solids (soluble salts), 600 parts per million.*
Chlorine, 30 parts per million.
Nitrogen in ammonium compounds (free ammonia), 0.1 part per million.
Nitrogen in readily oxidizable organic matter (albuminoid ammonia).
    High purity, 0.00 to 0.041 part per million.
    Satisfactory purity, 0.041 to 0.082 part per million.
    Impure, over 0.082 part per million.
Nitrogen as nitrates, 6 parts per million.
Nitrogen as nitrites, 0.02 part per million.
Phosphates, none allowed.

The matter of hardness relates more to proposed technical applications than to the sanitary value of a water; and, in regard to the quality of water for technical purposes, it may be said that the nearer the approach to purity the greater the advantage.

The following requirements of the United States Pharmacopœia for official water, which it defines as "natural water in its purest attainable state," will afford some idea of the properties of a highly pure water:

"A colorless, limpid liquid, without odor or taste at ordinary temperatures, and remaining odorless while being heated to boiling.

"Water should be perfectly neutral to litmus paper, and its transparency should not be affected, nor should any color be imparted to it, by hydrogen sulphide T. S., or ammonium sulphide T. S. (absence of metallic impurities).

"It should also remain unaffected by mercuric chloride T. S. (limit of ammonia).

"On evaporating 1000 c.c. of water on a water-bath, it should not leave a residue weighing more than 0.5 gm. (limit of soluble salts), and this residue, when ignited, should not carbonize, nor evolve ammoniacal or acid vapors.

"If 200 c.c. of water be acidulated with hydrochloric acid and heated to boiling, and 0.5 c.c. of barium chloride T. S.† added, the liquid, cooled and filtered, should give no further precipitate on the addition of a few drops of barium chloride T. S., even on standing (limit of sulphates).

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* Many otherwise pure artesian and mineral waters in constant use exceed this amount.

† Prepared by dissolving 12.2 gm. of pure, crystallized $BaCl_2.2H_2O$ in enough distilled water to make 100 c.c.

"If 200 c.c. of water be acidulated with nitric acid, and 0.5 c.c. of decinormal silver nitrate V. S. be added, the filtered liquid should not be affected by the subsequent addition of a few drops of silver nitrate T. S. (limit of chlorides).

"If 5 c.c. of water mixed with a few drops of diphenylamine T. S.* be carefully poured upon about 2 c.c. of sulphuric acid, free from nitrose,† contained in a test-tube, so as to form a separate layer, no blue color should be formed at the line of contact of the two liquids (limit of nitrates).

"If 100 c.c. of water be acidulated with diluted sulphuric acid free from nitrose, and a few drops of zinc-iodide-starch T. S.‡ subsequently added, the liquid should not at once assume a blue or violet color (absence of nitrites).

"On heating 100 c.c. of water, acidulated with 10 c.c. of diluted sulphuric acid, to boiling, and subsequently adding 0.5 c.c. of decinormal potassium permanganate V. S., the color of the liquid should not be completely destroyed by boiling it for ten minutes (limit of organic or other oxidizable matters)."

The following are the requirements of the United States Pharmacopœia for distilled water:

"A colorless, limpid liquid, without odor or taste, and perfectly neutral to litmus paper.

"The transparency of distilled water should not be affected, nor should any color be imparted to it, by test-solutions of hydrogen sulphide or ammonium sulphide (absence of metallic impurities), or by those of barium chloride (sulphates), silver nitrate (chlorides), ammonium oxalate (calcium), or mercuric chloride (ammonia); nor should its transparency be affected when mixed with twice its volume of calcium hydrate T. S. (absence of carbonic acid).

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* Prepared by dissolving 0.1 gm. of crystallized $(C_6H_5)_2NH$ in 50 c.c. of diluted sulphuric acid. The solution should be colorless.

† Nitric and nitrous acids. The absence of these impurities is established by the following tests. If 1 c.c. of diphenylamine T. S. be carefully poured, as a separate layer, upon 5 c.c. of sulphuric acid, contained in a test-tube, no distinct blue color should appear in the zone of contact (absence of nitric acid). If a few crystals of pyrogallol be dissolved in about 1 c.c. of pure water, and this solution be carefully poured, as a separate layer, upon some of the sulphuric acid, contained in a test-tube, no brown color should appear in the zone of contact (absence of nitric or nitrous acid).

‡ A few drops of fresh starch test-solution and a drop of potassium iodide test-solution may be substituted for the zinc-iodide-starch test-solution, if the last is not at hand.

"It should give no reaction for nitrates or nitrites when tested as described under water. [See page 303.]

"When 1000 c.c. of distilled water are evaporated on a water-bath to dryness, no residue should remain.

"On heating 100 c.c. of distilled water, acidulated with 10 c.c. of diluted sulphuric acid, to boiling, and subsequently adding 1 c.c. of centinormal potassium permanganate V. S., the color of the liquid should not be completely destroyed by boiling for ten minutes, nor by afterwards setting the vessel aside, well covered, for ten hours (absence of organic or other oxidizable matters)."

CHAPTER II.

MILK ANALYSIS.

THE essential constituents of milk are water, fat, proteids, milk-sugar, and salts. The proportion of these constituents varies in the milk of different animals.

The average composition of cow's milk approximates the following figures:

	Per Cent.
Fat	3.65
Proteids	4.40
Milk-sugar	4.25
Inorganic salts	0.75
Total solids	13.05
Water	86.95
Total	100.00

The composition of cow's milk varies according to the age, condition, breed, and food of the cow, and also to other circumstances.

The determinations of the total solids and fat usually suffice in the analysis of milk, although occasionally it is desired to know the amount of milk-sugar, proteids, and salts. The following simple process of analysis will give the quantity of each of these constituents. A platinum or porcelain dish about 4 or 5 centimeters in diameter is provided with a suitable glass rod rounded at the ends. The dish and rod are thoroughly dried, then allowed to cool, and accurately weighed together. 5 or 10 c.c. of the well-mixed milk are then put into the dish, and the total weight of dish, rod, and milk found as rapidly as possible, in order that the least amount of moisture may be lost from the milk through evaporation. The increase in weight represents the quantity of milk taken. The dish with its contents is now placed on a boiling water-bath that the water of the milk may evaporate. Towards the end of the evaporation the milk is stirred with the glass rod to produce a granular, porous residue. The heating is continued on the water-bath until the residue appears dry; the dish is then transferred to an air-bath and heated to 105° C. for one-half hour. At the end of this time it is allowed to cool, and is afterwards weighed. To make sure that the water is completely expelled, the dish is again heated in the air-bath, cooled, and weighed. When the weight is found to be constant, the quantity of *total solids* is ascertained by deducting the weight of the dish and rod from the weight of the dish, rod, and residue. The difference between the weight of milk taken and that of total solids represents, of course, the *water* of the milk.

To extract the *fat*, the residue of total solids is treated with several successive, small portions of ether, each portion being intimately mixed with the residue, and afterwards poured by decantation through a small, weighed, ashless filter into a weighed beaker. When this treatment is finished, the filter, with any particles of the insoluble residue, is put back into the dish, and the ether allowed to evaporate spontaneously; after which the dish and its contents are dried to a constant weight in the air-bath. If the weight of the dish, rod, insoluble residue, and filter is deducted from the weight of dish, rod, total solids, and filter, the difference will represent the *fat*. To check the result, the ethereal solution of the fat may be evaporated and the substance weighed directly.

The filter is removed from the dish and again placed in the funnel over a weighed beaker. The dried, fat-free residue is then treated on the water-bath with about 10 cubic centimeters of alcohol, the solvent being heated to boiling in contact with the residue. One-fourth an equal volume of boiling water is then carefully added from the wash-bottle, and the mixture thoroughly stirred with the rod. The clear, hot liquid is decanted upon the filter, and the treatment of the residue with the alcohol and water repeated twice in the foregoing manner. After the third application and filtration of the solvent, the filter is put back into the dish and the latter's contents thoroughly dried in the air-bath. The loss in weight by treatment with the weak alcohol shows the amount of *milk-sugar*. The result may be checked by evaporating the alcoholic solution to a constant weight, and, if deemed necessary, still further confirmed by titration with alkaline cupric tartrate volumetric solution, as described on page 196.

After extraction of the fat and milk-sugar the residue consists of proteids (albuminoids) and salts. The approximate estimation of the remaining substances is done by cautiously igniting the dish and its dried contents (rod, residue, and filter) at a dull red heat until all carbon is consumed. The residue in the dish then consists of the inorganic matter or *salts* of the milk. The amount of these is found by deducting the weight of dish and rod from the weight of dish, rod, and salts. If desired, the residue may be analyzed for the presence of added inorganic matter. The ash of normal milk is faintly alkaline. The principal constituents of the ash are the phosphates and chlorides of sodium, potassium, and calcium; traces of magnesium and iron are also usually present. The difference between the sum of the amounts of fat, milk-sugar, and salts and the weight of total solids equals the total *proteids* present. The total proteids may also be determined by the Kjeldahl method; this is done by placing in a flask a known weight (about 5 grammes) of milk, and proceeding, without evaporation, exactly as described on page 310 for the estimation of nitrogen. By multiplying the nitrogen found by 6.3, the amount of proteids in the weight of milk taken is obtained. The employment of the factor 6.3 is based on the composition of proteids in general; on an average they contain 15.88 per cent. of nitrogen; hence $100 \div 15.88 = 6.3$.

All the results are calculated into per cent. on the milk taken.

Where estimations of the total solids and fat only are required, the method of Adams is generally followed. This method consists in absorbing the milk in bibulous paper, evaporating the water, and extracting the fat in a Soxhlet apparatus. The paper used for this purpose should be free from substances soluble in the liquid to be used for extracting the fat. A paper manufactured especially for this purpose may be had of dealers in chemical supplies. The result for fat obtained through this method is somewhat higher than that yielded by the preceding method. Adams' method is most conveniently conducted as follows. A strip of the absorbent paper, about 5 or 6 centimeters wide and about 50 or 60 centimeters long, is tightly rolled round a small glass rod, the roll securely wrapped with white sewing-cotton, the latter tied, and the glass rod withdrawn. The roll of paper is then stood upon one of its ends in a dish, and, together with the latter, thoroughly dried in the air-bath at 105° C. When constant weight is attained, the roll of paper still being upon its end, about 5 cubic centimeters of the thoroughly mixed milk are carefully poured down a glass rod upon the upper end of the roll; the operation is to be conducted sufficiently slowly to permit complete absorption by the paper. Not more than about two-thirds of the roll should be moistened with the milk, and none of the latter should be allowed to come into contact with the dish, since only the paper will be subjected to treatment for the extraction of the fat. The dish and roll are again weighed; the increase in weight is the amount of milk taken. The vessel and its contents are put into the air-bath and dried at 105° C. till the weight remains unaltered. The difference between the weight at this point and that of the dish and roll equals the *total solids* of the portion of milk taken.

The roll is now inserted in a Soxhlet continuous extraction apparatus, the tared flask of which should have a capacity of about 150 cubic centimeters, and contain about 75 cubic centimeters of ether, or of petroleum spirit boiling at 45° C. Heat is applied to the flask by means of a water-bath, and the extraction conducted for three hours. At the end of that time the flame is extinguished, the flask detached, the ether removed by distillation, and the fat dried by heating in an air-bath at 105° C. During the drying, air is occasionally blown into the flask to expel the ether vapor. When a constant weight is reached, the weight of the flask subtracted from that of the flask and fat leaves the weight of the *fat* in the quantity of milk taken.

The ether used for the extraction of the fat should be previously dried by means of calcium chloride and then rectified.

Sour milk must be thinned with a definite quantity, by weight, of ammonium hydrate before taking the portion for analysis; allowance must, of course, be made for the dilution.

Human milk can be analyzed by the methods employed for cow's milk. According to Lehmann and Hempel, human milk has the following composition:

	Per Cent.
Fat	3.80
Proteids	1.70
Milk-sugar	6.00
Inorganic salts	0.20
Total solids	11.70
Water	88.30
Total	100.00

CHAPTER III.

THE ESTIMATION OF NITROGEN.*

As it is sometimes desirable to estimate the nitrogen contained in organic substances independently of an ultimate analysis, the following methods are here given :

SODA-LIME METHOD.

This method of estimating nitrogen in organic substances is applicable in all cases in which that element does not exist as a nitrate. The adaptability of the process lies in the fact that, when strongly heated with an alkali hydrate, nitrogenous organic substances evolve their nitrogen as ammonia. The latter is absorbed in oxalic or sulphuric acid volumetric solution. The percentage of nitrogen is calculated from the amount of acid neutralized by the ammonia. This is determined by using a definite volume of the acid solution, which is known to be an excess, and, after the absorption of the ammonia, titrating the remaining acid with standard alkali.

The analysis is conducted by mixing the substance to be estimated with soda-lime (a granulated mixture of sodium hydrate and calcium oxide) and heating the mixture in a combustion-tube, some unmixed soda-lime being previously placed at both ends of the column of the mixture, and the whole secured in place by plugs of asbestos.

The tube is placed in a combustion-furnace, and heated to redness a few inches back of the anterior end, to which a Varrentrapp and Will's absorption bulb, containing a convenient known quantity of the standard acid, has been attached. The heat is then gradually extended along the tube to the posterior end. When absorption no longer occurs, and the contents of the bulb recede, this end is broken off, and air drawn through the tube by suction applied to the absorption bulb ; a rubber tube is attached to the latter for this purpose. By the last treatment all traces of ammonia are absorbed. The contents of the bulb are now transferred to a beaker, the bulb rinsed with water, the rinsings poured into the beaker, and the contents of the latter titrated with standard alkali; cochineal or rosolic acid test-solution is used as indicator. Each cubic centimeter of normal acid volumetric solution which is neutralized by the ammonia indicates 0.01401 gramme of nitrogen.

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* The subjects of the ultimate analysis of organic compounds and of the determination of vapor density are treated in Volume I. pages 522 and 528.

Liquid nitrogenous compounds are weighed in small, sealed, glass bulbs, which are to be placed in a layer of soda-lime.

If the substance is rich in nitrogen some cane-sugar should be mixed with it, so that there may be some non-nitrogenous gases to dilute the ammonia.

THE KJELDAHL METHOD.

This method, which has largely superseded the soda-lime process for the estimation of nitrogen, is founded on the fact that complete oxidation of organic substances takes place when they are digested with concentrated sulphuric acid and potassium permanganate. The nitrogen is converted into ammonia, which at once combines with the excess of acid.

The following outline of the method is taken from the Official Methods of Analysis adopted by the Association of Official Agricultural Chemists at its meeting in August, 1894. .7 to 3.5 gm. of the substance to be analyzed (according as the amount of nitrogen is likely to be much or little) are brought into a flask with an equal weight of yellow mercuric oxide, which hastens the oxidation, and 20 c.c. of sulphuric acid (sp. gr. 1.84). The mixture is then heated below the boiling point of the acid for from 5 to 10 minutes, or until frothing has ceased; to stop excessive frothing a small piece of paraffin may be added.

The heat is now increased until the acid boils, and the contents of the flask have become clear and colorless, or nearly so. Powdered potassium permanganate, in small quantities at a time, is now carefully dropped in until, after shaking, the liquid remains of a green or purple color. After cooling, 200 c.c. of water are added. To prevent bumping during distillation, a few pieces of granulated zinc are introduced into the flask, and 1 gm. of potassium sulphide in solution is added with the view of obviating the formation of mercuro-ammonium compounds. 50 c.c. of saturated solution of sodium hydrate, or sufficient to make the mixture alkaline, are next added by pouring the same down the side of the flask so that it does not mix at once with the acid solution. The flask is then connected with a condenser, one end of which is inserted into another flask containing a definite volume of standard acid.

The contents of the distilling flask are now mixed by shaking, and then distilled until all of the ammonia has passed over into the standard acid. The first 150 c.c. of the distillate will generally contain all of the ammonia. The contents of the receiving flask are then titrated with standard alkali, cochineal test-solution being used as an indicator.

The result is calculated from the amount of acid neutralized by the distillate.

Each cubic centimeter of normal acid volumetric solution which is neutralized by the ammonia indicates 0.01401 gramme of nitrogen.

The apparatus and the quantities of reagents used in the estimation should be tested by a blank experiment with some non-nitrogenous substance, such, for instance, as sugar; if nitrogen is found, a correction should be applied for its amount.

The foregoing treatment does not effect the estimation of nitrogen when the latter is present as nitrates.

To include the nitrogen of these compounds, the method may be modified as follows:

.7 to 3.5 gm. of the substance are well mixed with 30 c.c. of sulphuric acid (sp. gr. 1.84) and 1 gm. of salicylic acid; 5 gm. of crystallized sodium thiosulphate are then added. The last two substances may be replaced by 2 gm. of salicylic acid and 2 gm. of zinc-dust. The flask is heated over a low flame until all danger from frothing has passed; then the heat is raised until the mixture boils briskly, and continued until white fumes no longer issue from the flask. This requires about five or ten minutes.

A quantity of yellow mercuric oxide equal to the substance taken is now added, and the boiling continued until the liquid in the flask is colorless, or nearly so.

Additional sulphuric acid should be supplied if the contents of the flask show indications of becoming solid.

The oxidation is completed with potassium permanganate in the usual way, and from this point the operation is conducted according to the regular method.

Since the institution of the Kjeldahl method, many variations in the details of the process have been suggested with a view to shortening the time required for the digestion with the sulphuric acid. Prominent among those which have thus far met with general approbation is

THE GUNNING METHOD.

This differs from that of Kjeldahl in the replacement of the yellow mercuric oxide by 10 grammes of powdered potassium sulphate, which is added in portions to the hot mixture of the substance to be estimated and the usual amount of the sulphuric acid. The boiling point of the acid is raised by this addition, and the oxidation of the organic matter thereby rendered complete without the aid of potassium permanganate, which is consequently dispensed with.

By omitting the mercuric oxide, the use of potassium sulphide also becomes unnecessary.

The liberation of the ammonia, the distillation, and the titration are conducted as in the Kjeldahl method.

APPENDIX.

TABLE OF ATOMIC WEIGHTS ACCORDING TO THE U. S. PHARMACOPŒIA, TOGETHER WITH VALENCES.

NAME.	Symbol.	Atomic Weight.	Valence.
Aluminum	Al	**27.04**	III or $(Al_2)^{VI}$
Antimony	Sb	**119.6**	III, V
Arsenic	As	**74.9**	III, V
Barium	Ba	**136.9**	II, IV
Beryllium *	Be	**9.03**	II
Bismuth	Bi	**208.9**	III, V
Boron	B	**10.9**	III
Bromine	Br	**79.76**	I, III, V, VII
Cadmium	Cd	**111.5**	II
Cæsium	Cs	**132.7**	I
Calcium	Ca	**39.91**	II, IV
Carbon	C	**11.97**	IV
Cerium	Ce	**139.9**	$(Ce_2)^{VI}$, IV
Chlorine	Cl	**35.37**	I, III, V, VII
Chromium	Cr	**52.0**	II, $(Cr_2)^{VI}$, VI
Cobalt	Co	**58.6**	II, $(Co_2)^{VI}$
Columbium †	Cb	**93.7**	III, V
Copper	Cu	**63.18**	$(Cu_2)^{II}$, II
Didymium ‡	Di	**142.0**	III, V
Erbium	Er	**166.0**	III or $(Er_2)^{VI}$
Fluorine	F	**19.0**	I
Gallium	Ga	**69.9**	$(Ga_2)^{VI}$
Germanium	Ge	**72.3**	II, IV
Gold	Au	**196.7**	I, III
Hydrogen	H	**1.0**	I
Indium	In	**113.6**	III or $(In_2)^{VI}$
Iodine	I	**126.53**	I, III, V, VII
Iridium	Ir	**192.5**	II, IV
Iron	Fe	**55.88**	II, $(Fe_2)^{VI}$, VI
Lanthanum	La	**138.2**	III
Lead	Pb	**206.4**	II, IV
Lithium	Li	**7.01**	I
Magnesium	Mg	**24.3**	II
Manganese	Mn	**54.8**	II, IV, VI, VIII
Mercury	Hg	**199.8**	$(Hg_2)^{II}$, II
Molybdenum	Mo	**95.9**	II, IV, VI
Nickel	Ni	**58.6**	II, $(Ni_2)^{VI}$
Nitrogen	N	**14.01**	I, III, V
Osmium	Os	**190.3**	II, IV, VI, VIII

* Also called Glucinum, Gl = 9.03.

† Also called Niobium, Nb = 93.7.

‡ Composed of Neo- and Praseo-Didymium.

TABLE OF ATOMIC WEIGHTS ACCORDING TO THE U. S. PHARMACOPŒIA, TOGETHER WITH VALENCES.—(*Continued.*)

NAME.	Symbol.	Atomic Weight.	Valence.
Oxygen	O	**15.96**	II
Palladium	Pd	**106.35**	II, IV
Phosphorus	P	**30.96**	III, V
Platinum	Pt	**194.3**	II, IV
Potassium	K	**39.03**	I
Rhodium	Rh	**102.9**	II, IV
Rubidium	Rb	**85.2**	I
Ruthenium	Ru	**101.4**	II, IV, VI, VIII
Samarium	Sm	**149.62**	III, V
Scandium	Sc	**43.97**	III or $(Sc_2)^{VI}$
Selenium	Se	**78.87**	II, IV, VI
Silicon	Si	**28.3**	IV
Silver	Ag	**107.66**	I
Sodium	Na	**23.0**	I
Strontium	Sr	**87.3**	II, IV
Sulphur	S	**31.98**	II, IV, VI
Tantalum	Ta	**182.0**	III, V
Tellurium	Te	**125.0**	II, IV, VI
Terbium	Tb	**159.1**	III
Thallium	Tl	**203.7**	I, III
Thorium	Th	**231.9**	IV
Tin	Sn	**118.8**	II, IV
Titanium	Ti	**48.0**	IV
Tungsten	W	**183.6**	II, IV, VI
Uranium	U	**238.8**	II, IV, VI
Vanadium	V	**51.1**	III, V
Ytterbium	Yb	**172.6**	III
Yttrium	Yt	**88.9**	III
Zinc	Zn	**65.1**	II
Zirconium	Zr	**90.4**	IV

ALCOHOL.

ACCORDING TO E. R. SQUIBB.

Specific Gravity at 15.555° C. (Pure water at 15.555° C. (60° F.) taken as unity.)	Percentage.				Specific Gravity at 15.555° C. (Pure water at 15.555° C. (60° F.) taken as unity.)	Percentage.				Specific Gravity at 15.555° C. (Pure water at 15.555° C. (60° F.) taken as unity.)	Percentage.			
	Absolute Alcohol.					Absolute Alcohol.					Absolute Alcohol.			
	By weight.	By volume.	Under proof. (Brit. Excise.)	Of proof spirit. (U.S. Revenue.)		By weight.	By volume.	Under proof. (Brit. Excise.)	Of proof spirit. (U.S. Revenue.)		By weight.	By volume.	Under proof. (Brit. Excise.)	Of proof spirit. (U.S. Revenue.)
1.0000					0.9794			71	33	0.9555			34	75
0.9993			99	1	0.9789	14	17	70	34	0.9550		38	33	76
0.9985		1	98	2	0.9784			69	35	0.9544	32			77
0.9981	1				0.9778	15	18	68	36	0.9539			32	
0.9976			97	3	0.9775				37	0.9535		39		78
0.9970		2		4	0.9772			67	38	0.9528	33		31	79
0.9968			96		0.9766	16	19	66	39	0.9519		40	30	80
0.9965	2			5	0.9760		20	65	40	0.9511	34		29	81
0.9960			95		0.9753	17	21	64	41	0.9503		41	28	82
0.9956		3		6	0.9749			63	42	0.9495			27	83
0.9952			94		0.9743			62	43	0.9490	35	42		84
0.9947	3			7	0.9741	18	22		44	0.9485			26	
0.9944			93		0.9737			61	45	0.9475			25	85
0.9942		4		8	0.9732			60	46	0.9470	36	43		86
0.9936			92	9	0.9728	19	23	59	47	0.9465			24	
0.9930	4	5	91	10	0.9720			58	48	0.9455			23	87
0.9921			90	11	0.9716	20	24		49	0.9452	37	44		88
0.9914	5	6	89	12	0.9714			57	50	0.9446			22	89
0.9906			88	13	0.9709		25	56		0.9434	38	45	21	90
0.9900			87		0.9704	21		55	51	0.9426			20	91
0.9898	6	7		14	0.9698		26	54	52	0.9416	39	46	19	92
0.9892			86	15	0.9693				53	0.9405			18	93
0.9890		8		16	0.9691	22	27	53	54	0.9396	40	47	17	94
0.9885			85		0.9683			52	55	0.9391				95
0.9884	7			17	0.9678	23	28	51	56	0.9381		48	16	96
0.9878		9	84	18	0.9671			50	57	0.9376	41			
0.9872			83	19	0.9665	24	29	49	58	0.9373			15	97
0.9869	8	10		20	0.9658			48	59	0.9362		49	14	98
0.9864			82	21	0.9652	25	30	47	60	0.9356	42			
0.9857			81		0.9645			46	61	0.9352			13	99
0.9855	9	11		22	0.9643		31		62	0.9343		50	12	100
0.9852			80	23	0.9638	26		45	63	0.9335	43			101
0.9845			79		0.9631		32	44	64	0.9329			11	
0.9841	10	12		24	0.9623	27		43	65	0.9323		51		102
0.9838			78	25	0.9618		33	42	66	0.9318			10	
0.9831			77	26	0.9609	28	34	41	67	0.9314	44			103
0.9828	11	13		27	0.9602			40	68	0.9306			9	
0.9825			76		0.9595			39	69	0.9303		52		104
0.9821		14		28	0.9593	29	35		70	0.9292	45		8	105
0.9819			75		0.9587			38	71	0.9283		53	7	106
0.9815	12	15		29	0.9578	30	36	37	72	0.9270	46		6	107
0.9813			74	30	0.9572			36	73	0.9262		54	5	108
0.9807			73	31	0.9565		37	35		0.9249	47		4	109
0.9802	13	16	72	32	0.9560	31			74	0.9242		55		110

ALCOHOL.—(*Continued.*)

Specific Gravity at 15.555° C. (Pure water at 15.555° C. (60° F.) taken as unity.)	Percentage.				Specific Gravity at 15.555° C. (Pure water at 15.555° C. (60° F.) taken as unity.)	Percentage.				Specific Gravity at 15.555° C. (Pure water at 15.555° C. (60° F.) taken as unity.)	Percentage.			
	Absolute Alcohol.		Under proof. (Brit. Excise.)	Of proof spirit. (U.S. Revenue.)		Absolute Alcohol.		Over proof. (Brit. Excise.)	Of proof spirit. (U.S. Revenue.)		Absolute Alcohol.		Over proof. (Brit. Excise.)	Of proof spirit. (U.S. Revenue.)
	By weight.	By volume.				By weight.	By volume.				By weight.	By volume.		
0.9236			3		0.8850		72		144	0.8396			55	176
0.9228	48			111	0.8840	65		27	145	0.8387				177
0.9221		56	2	112	0.8825		73	28	146	0.8382	84			
0.9212			1	113	0.8816	66				0.8376			56	
0.9206	49				0.8811			29	147	0.8373		89		178
0.9200		57	Proof over.	114	0.8799		74	30	148	0.8357	85		57	179
0.9189			1	115	0.8793	67			149	0.8340		90		180
0.9184	50				0.8783			31		0.8336			58	
0.9178		58	2	116	0.8769	68	75	32	150	0.8331	86			
0.9168				117	0.8754			33	151	0.8317			59	181
0.9160	51	59	3	118	0.8745	69	76		152	0.8305	87	91		182
0.9150			4	119	0.8739			34	153	0.8298			60	
0.9135	52	60	5	120	0.8721	70	77	35	154	0.8288				183
0.9124			6	121	0.8708			36	155	0.8279	88		61	
0.9113	53	61	7	122	0.8696	71	78	37		0.8272		92		184
0.9100			8	123	0.8693				156	0.8259			62	
0.9090	54	62	9	124	0.8678			38	157	0.8254	89			185
0.9075			10	125	0.8672	72			158	0.8240			63	
0.9069	55	63		126	0.8664		79	39		0.8237		93		186
0.9062			11	127	0.8649	73			159	0.8228	90			
0.9047	56	64	12	128	0.8646			40		0.8221			64	187
0.9036			13		0.8639		80		160	0.8199	91	94	65	188
0.9025	57	65		129	0.8631			41		0.8176			66	189
0.9021			14	130	0.8625	74				0.8172	92			
0.9008			15	131	0.8615			42	161	0.8164		95		190
0.9001	58	66		132	0.8611		81		162	0.8156			67	
0.8994			16	133	0.8603	75			163	0.8145	93			
0.8979	59		17		0.8599			43		0.8139				191
0.8973		67		134	0.8581	76	82	44	164	0.8134			68	
0.8966			18		0.8566			45	165	0.8125		96		
0.8956	60			135	0.8557	77	83			0.8118	94			192
0.8953			19		0.8550			46	166	0.8112			69	
0.8949		68		136	0.8539				167	0.8098				193
0.8938			20	137	0.8533	78		47		0.8090			70	
0.8932	61				0.8526		84		168	0.8089	95			
0.8925		69	21	138	0.8516			48		0.8084		97		194
0.8910			22	139	0.8508	79			169	0.8061	96			195
0.8908	62				0.8501			49	170	0.8041		98		196
0.8900		70		140	0.8496		85			0.8031	97			
0.8897			23		0.8483	80		50	171	0.8014				197
0.8886	63			141	0.8466		86	51	172	0.8001	98			
0.8883			24		0.8459	81				0.7995		99		
0.8875		71		142	0.8450			52	173	0.7992				198
0.8869			25		0.8434	82	87	53	174	0.7969	99			199
0.8863	64			143	0.8415			54	175	0.7946		100		200
0.8854			26		0.8408	83	88			0.7938	100			

RULES FOR MAKING AN ALCOHOL OF ANY REQUIRED LOWER PERCENTAGE FROM AN ALCOHOL OF ANY GIVEN HIGHER PERCENTAGE. (ACCORDING TO THE UNITED STATES PHARMACOPŒIA.)

I. **By Volume.**—Designate the volume-percentage of the stronger alcohol by V, and that of the weaker alcohol by v.

Rule.—Mix v volumes of the stronger alcohol with pure water to make V volumes of product. Allow the mixture to stand until full contraction has taken place, and until it has cooled, then make up any deficiency in the V volumes by adding more water.

Example.—An alcohol of 30 per cent. by volume is to be made from an alcohol of 94 per cent. by volume.—Take 30 volumes of the 94 per cent. alcohol, and add enough pure water to produce 94 volumes.

II. **By Weight.**—Designate the weight-percentage of the stronger alcohol by W, and that of the weaker alcohol by w.

Rule.—Mix w parts by weight of the stronger alcohol with pure water to make W parts by weight of product.

Example.—An alcohol of 50 per cent. by weight is to be made from an alcohol of 91 per cent. by weight.—Take 50 parts by weight of the 91 per cent. alcohol, and add enough pure water to produce 91 parts by weight.

Explanatory Note.—In stating the required results of volumetric analyses, the United States Pharmacopœia frequently uses the preposition *about;* the variation allowed by this authority, in such cases, is 2 per cent. of the stated amount, either way from that amount: thus, the expression about 25 c.c. is to be interpreted as standing for 24.5 to 25.5 c.c.

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